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TECHNICAL REPORT III

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REACTION OF NaK AND H₂O

by

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February 1, 1950

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ABSTRACT

A report is presented on the progress made to date for the reaction of both superheated steam and liquid water with liquid sodium-potassium alloy of 66 Wgt. % K composition. The conclusion is drawn, after assuming certain conditions, that the reaction of NaK and superheated steam is of little hazard. A method is suggested for controlling the amount of damage that is possible in the reaction of NaK and liquid water.

A rough approximation is also presented of the theoretical adiabatic and isothermal reactions of Na and H_2O assuming a completely filled and rigid container.

INTRODUCTION

If sodium-potassium alloys (referred to as NaK) are to be used to any great extent as a heat transfer medium for the production of steam, a study must be made to determine the hazard involved should a leak or break occur in the heat exchanger. It is assumed that in order to obtain superheated steam two exchangers will be used; one for the evaporation of the liquid water, the other for superheating the steam after it leaves a separator which connects the two units.

Keeping this arrangement of exchangers in mind, a series of tests were made using steam and liquid water with NaK, the results of which as yet are not conclusive; however, the information obtained to date is of enough importance to warrant a report on the progress made thus far.

The tests made to date fall into eight series; each series is an attempt to study some different phase. The eight series of runs are as follows and will be presented separately.

1. The reaction of NaK and superheated steam.
2. The first series of runs using NaK and liquid water.
3. The reaction of NaK and liquid water in a closed container with a known interface.
4. The first attempt to determine the effect of the pressure front created by the reaction.
5. A series of tests measuring pressure at four points on an extended system.
6. A series of tests on a simple reactor to determine the effect of position, pressure and speed of the opening device.
7. Second attempt to determine the effect of the pressure front created by the reaction.
8. Third attempt to determine the effect of the pressure front created by the reaction.

All pressure measurements were made with electronic equipment supplied by Electro Products Corporation. This equipment consists of a pressure pickup, a pressuregraph, an oscillograph, and a camera. A current of high frequency is sent to the pressure pickup which consists of two flat plates, one being grounded. The grounded plate is a flat diaphragm which, when stressed by the pressure inside the chamber, changes its shape, thereby changing the distance

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between the two plates and causing a variation in the capacitance of the pickup. This variation is picked up in the pressuregraph and sent into the oscillograph. The resulting beam on the cathode ray tube shows up as a line whose change in width indicates a change in pressure.

EXPERIMENTAL UNITS AND RESULTS

The description, procedure and results of the eight series of runs are presented in order.

1. The reaction of NaK and superheated steam. This series of runs was made in equipment shown in Figure 1A. The upper and lower chambers were made from type 347 standard 4" stainless steel pipe. The intermediate plate, as shown, contained a 1/2" orifice. The pressure pickups were located at the extreme ends as shown. The two chambers were separated one from another by a plunger which seated on the sharp edge of the orifice. This plunger was released by a trigger mechanism which set into operation a system of springs which in turn pulled the plunger from its seat.

The equipment, after first being evacuated, was charged with approximately 2½ pounds of NaK in the top chamber and a small amount of water in the bottom chamber. Both chambers were heated electrically. Steam is bled from the bottom chamber until the desired degree of temperature and pressure was reached to insure approximately 15° superheat. The pressure in the steam chamber was set higher than that in the reaction chamber so that when the plunger was pulled the steam would bubble up through the NaK. Three runs were made at different pressures. The results showed an overall decrease in the final pressure as would have been predicted by the gas law taking into consideration the chemical change and the heat of reaction from the following equation:



From the equation it can be seen that the volume that was once occupied by one mol of steam is occupied after the reaction by only 1/2 mol of hydrogen.

An example is the third run of this series with the steam at 200 p.s.i. gauge and 15° superheat. By theoretical calculations the resulting pressure in the system should be 79 p.s.i., while that experienced at the end of the run was 85 p.s.i. A pressure time plot of both the pressure in the NaK and steam chambers is shown in Figure 2.

The time for the reaction is, however, not indicative of the speed of the reaction itself, but is limited by the orifice in its ability to allow the NaK and the steam to mix. A run was made using nitrogen in place of the steam, and the time

required until equilibrium or equal pressures were obtained in both chambers was only 16% less for the nitrogen run than that experienced when using steam. A more complete description is given in a previous report. (1)

From the information thus far collected on superheated steam it is concluded that should a leak or break occur in the superheater little or no damage would result from the reaction itself, and the highest pressure that would be obtained would be the pressure of the steam entering the exchanger.

2. The first series of runs using NaK and liquid water. This series of water runs was made in the same type equipment as the steam runs except that all external connections in the bottom or water chamber were moved from the end plate to the side in order to eliminate any pockets that might hinder the reaction. The equipment was filled in the same manner as before with 2½ pounds of NaK in the top chamber and a measured quantity of water in the lower chamber. The nitrogen over the NaK was at approximately 30 p.s.i. pressure while the only pressure in the water chamber was the vapor pressure of the water itself at room temperature. When the trigger was fired, the NaK was forced through the 1/2" orifice into the water chamber where it traveled approximately one foot onto the water at the bottom.

The orifice, as in the steam runs, was again a limiting factor in that it would allow only a part of the NaK necessary to complete the reaction to come in contact with the water at any given time. Due to the evolution of H₂ by the reaction a system of unbalanced pressure was set up which would oscillate between the two chambers causing the NaK to contact the water in spurts, which would continue until a sufficient quantity of NaK was obtained to react all the water.

In the third run of the series with 200 c.c. of water in the chamber, the time for complete reaction was approximately six seconds. A plot of this run, Figure 3, shows the stepwise increase in pressure and gives the first evidence that even through the actual chemical reaction of NaK and water is extremely fast, the time of complete reaction is relatively slow because the two are continually being separated by the hydrogen gas given off every time the two reactants make contact. A complete description of this series is given in a previous report. (1)

3. The reaction of NaK and liquid water in a closed container with a known interface. Since the orifice, in both size and position, was the limiting factor in the first series of water runs, a new setup was made with a small NaK chamber on the bottom on which the plunger seated over the entire diameter of the chamber. The NaK chamber was completely filled while the water covered the seat from above so that, when the plunger was pulled, the NaK and the water came into immediate contact. A sketch of this reactor is shown in Figure 4. The

NaK chamber was made of standard 1" pipe with the inside diameter carrying up through the flange to the sharp edged seat making the total chamber length three inches. After it had been evacuated, it was completely filled with NaK through the 1/4" pipe on the bottom. A 1/4" pipe tap was located on the side for a pressure pickup. The upper or water chamber was made of 4" pipe eight inches long with two 1" pipe outlets on each side. The pressure pickup and the 1/4" filling line was located on the top. After evacuating, the water chamber was filled completely with the exception of a small nitrogen space.

Four runs were made in this series. The first two with the two 1" pipe outlets capped, the last two with a Black, Sivals, and Bryson safety head flange on one outlet using a 1500 p.s.i. blowout disc.

The first two runs of this series gave no significant results; the peak pressure was about 10% greater than the final pressure, and the time of complete reaction was a little over 1 1/2 seconds. See Figure 5 for an example. The film showed irregular marks at the points of reaction similar to marks made by sound waves.

The last two runs with the 1500 p.s.i. blowout disc complicated the picture in that the discs broke, and at no time was the static pressure higher than 20-30 p.s.i. as measured by the pressure pickup. However, the irregularities (See Figure 6) at the points of reaction on the film strip were markedly increased. This irregularity was at first thought to be shock waves; but since they were not definitely understood in this case and do not conform completely to the conception of a shock wave, hereafter they will be referred to as a pressure front or the surge of pressure transmitted through the liquid by a molecular vibration, while pressure existing in a static state is referred to as static pressure.

4. The first attempt to determine the effect of the pressure front created by the reaction. In this set of runs an expansion tank was added to the equipment. The addition was made by connecting 1" standard black iron pipe to the 1" outlet on the side of the water chamber, and, after making two right angle bends, was attached to the bottom of an expansion tank, which consisted of 2 feet of 4" pipe. See Figure 7 and accompanying notes. Thereafter the equipment is referred to as being in two parts, the reactor and the expansion tank, the reactor being the NaK and water chamber and the expansion tank the section of 4" pipe overhead. In the first set of runs of this series a valve was in the position shown in the drawing; in the second set of runs it was replaced by a length of 12 pipe.

The blowout discs that were ruptured in Series 3, even though they were 1500 p.s.i. discs, were extremely thin, .006 inches, and made of stainless steel. This thinness does not facilitate much shock absorption since they are quite rigid and have very little mass.

The General Electric Company requested that a bellows valve be tested and results obtained compared to those of rupture discs. The valve was put into the system and two reactions run. In both runs the remaining 1" outlet on the reactor was capped and a 120 p.s.i. blowout was placed on the expansion tank. After evacuating, both the NaK and water chambers (including the expansion tank) were filled completely with their respective materials. From the expansion tank 500 c.c. of water was removed and replaced by nitrogen at atmospheric pressure.

For the first run nitrogen was forced into the uppermost part of the reactor with sufficient pressure to reduce the volume of free space in the expansion tank to 250 c.c., thus obtaining an equal volume in both the reactor and the expansion tank. For the second run no nitrogen space was in the reactor, but the entire free space was in the expansion tank. The 120 p.s.i. rupture disc on the expansion tank ruptured readily. The results of both runs showed no measurable effect on the bellows. The flexibility of the bellows was probably sufficient to absorb any shock that was present.

The next question that arose, also coming from General Electric Company, was whether the rupturing of a blowout disc in the immediate vicinity of the reaction had any effect on a second disc some distance away. This problem was approached by two methods, neither with much success. The first was dealt with by the equipment shown in Figure 7; the other will be discussed later under Series 5.

The ratings of the blowout discs used on the reactor and expansion tank were varied to study their effect. Three runs were made; the first with a 500 p.s.i. disc on both the reaction and expansion chambers; the second with a 500 p.s.i. disc on the reaction chamber and a 1,000 p.s.i. disc on the expansion tank; and the third run had a 1,000 p.s.i. disc on the reaction chamber and a 500 p.s.i. disc on the expansion tank. The results were disappointing because in the first run both discs blew and in the succeeding runs none of the discs ruptured.

It was at this point that it became evident that the reaction was not going to completion in the same way every time. A section of the film strip for one of the runs is shown in Figure 8. This picture shows the so-called pressure front set up by the reaction and the resulting pressure caused by the flow of water upward into the expansion tank. The peak pressure of highest point seen in the photograph in the reactor, was 550 p.s.i. while in the expansion tank the peak pressure was 780. As a result of the kinetic energy in the fluid flowing away from the reactor and through the 1" pipe, it is not surprising that the pressure in the expansion tank had a higher peak.

The entire water system was, for the first time, completely filled with the exception of a small space in the expansion tank during this series of runs. It would follow from the above fact that it is quite possible to relieve the pressure generated in the vicinity of the reaction. In the system used, the liquid and liberated gases moved away from the point of the reaction through the prepared piping which made two right angle bends without damage to the equipment.

5. A series of tests measuring pressure at four points on an extended system. The system using four pickups at various parts of an extended system was actually run immediately after the runs using the valve supplied by General Electric, but due to the individuality of the system it is considered separately. This system was also suggested by the General Electric Company and again gave meager results. These experiments were set up using the expansion tank mentioned before and a system of 1" pipe as shown in Figure 9. The object of this plan was to determine the ability of the pressure front to damage blowout diaphragms placed at different points in the system. The pressure pickups were located as near the blowout disc as possible. Three runs were made in this manner. In the first run the system was completely filled with water except for a 500 c.c. nitrogen space in the expansion tank. The reaction was set off, and none of the 1500 p.s.i. blowout discs ruptured. The system was then drained and dried and refilled, this time utilizing a 250 c.c. nitrogen space in the expansion tank, with no change in rupture disc. The rupture disc on the expansion tank and on the reactor end of the 15 foot length of pipe broke, leaving only the other disc intact. It was discovered that the remaining disc was deformed. This deformation gave rise to the question of whether all the discs in the first reaction had not been deformed before the second run was made. The third run was a duplicate of the second using all new blowout discs, and none of them ruptured.

In the second reaction it was noted on the film strip that a sort of reflection or repeating of the pressure front recurred four or five times on the trace obtained from the pickup at the extreme end of the 15 foot length of pipe. This fact was at first attributed to reflections of a shock wave; however, when the speed of the wave was calculated using the longest path possible, it was found to have traveled only about 2760 ft/sec while a shock wave must travel at least the speed of sound or approximately 5000 ft/sec in water. (2)

6. A series of tests on a simple reactor to determine the effect of position, pressure and speed of the opening device. The runs of Series 4 and 5 were attempts to solve too many problems at one time with too little fundamental knowledge. It was decided then to go to a more simple system (Figure 10) over which greater control of the factors thought to be variables might be exerted. It was

pointed out in Series 4 that the reaction was not reproducible. It was thought that perhaps the trigger mechanism was not pulling the plunger back off the seat with the same speed in every run. To check the speed, coils of 136-200 turns were attached to the piston that drives the plunger back. The coils were pulled through a magnetic field and the e.m.f. generated was put on one trace of the oscillograph. The piston travels approximately $1/3$ its total distance before it engages the plunger. The pattern shown in Figure 11 shows this trace. The point of contact of the piston and the plunger and also the stop that ended the travel of both can be observed. Only one pressure measurement, which was taken from a pickup located on the reaction chamber, was made in each of the runs.

Ten runs were made in this series, all of which had a similar trigger trace thus eliminating the idea that the variations in the different reactions was due to the unpredictability of the trigger mechanism.

The runs were made in four groups, three with the equipment right side up or with the NaK on the bottom, three with the equipment upside down with the NaK on the top, two with the equipment on its side with the NaK chamber horizontal, and two with the equipment right side up with an initial pressure of 400 p.s.i. on the entire system.

Change of position showed little difference in the reaction rates as compared one with another. The upside down runs were slightly faster. The runs with the initial 400 p.s.i. pressure showed none of the irregularities, referred to as pressure front, that have been seen in the atmospheric pressure runs heretofore.

The time of complete reaction of all the runs was in the same order. For a period of 1 to $1\frac{1}{2}$ seconds after the plunger came off its seat there was little change in static pressure after which time the pressure rose to its static peak in approximately $1/4$ to $1/2$ seconds. This pressure change during the reaction appeared to be independent of the position of the reactor and of the initial pressure on the equipment.

Another test was made to try to see visually what happened during the reaction. For this test a 1" pipe nipple three inches long was capped at one end making a container that was later filled with NaK. The top of the container was covered with a very porous paper to prevent spilling. The container was then thrown into a pond and the effect observed. When the pipe hit the water a sharp and short report was observed and then from under the water a steady stream of small bubbles arose and continued for approximately two seconds.

This series of runs was of great value in that some of the questions as to the peculiarities of this individual system were answered. The fact that in ten runs there was little or no difference evident in the trigger trace almost eliminates this as a factor in the non-reproducibility of the reaction. The fact that the position had little effect on the reaction may be peculiar to this system only.

The runs with an initial pressure of 400 p.s.i. indicate that the size of the "gas bubble" has considerable effect on the pressure front but has little effect on the complete reaction. A discussion of this "gas bubble" effect will be presented in a later section of this report.

7. Second attempt to determine the effect of the pressure front created by the reaction. This series of runs was an attempt to separate the effect of the pressure front and of the static pressure build up. To estimate the effects, so-called test sections were made by flattening 3/4" O.D. tubing of .035" wall to 1/2" outside measurements for a length of 2". See Figure 12. This flattened section was plugged at one end and silver soldered at the other to a standard 1" pipe cap. A number of these test sections were made up all from the same section of tubing. One test section was then subjected to 200, 400, 600, 800, 1000 p.s.i. pressure. Before and after each pressure, the dimensions of the piece were measured to determine the permanent set in the section caused by the static pressure. The dimension measurements of the piece were made by gauging the thickness at three points along the 2" flattened part and by measuring the volume. The changes in the thickness and volume were plotted against the pressure causing the change and a smooth curve drawn connecting the points. The remaining test sections were placed on the equipment one at a time and the equipment fired. From the change in thickness and volume the effective pressure could be determined that had been in the test section. Knowing the actual peak static pressure that was in the equipment as indicated by the film strip, it has to follow that any discrepancy between the two must be due to the pressure front.

Twelve runs have been made starting at atmospheric pressure, which are in three classifications. Figure 13 shows the setup for all the runs in this section except the second classification. The first three runs were made after filling the equipment with water and then draining 375 c.c. from the expansion tank and at the same time replacing it with nitrogen at atmospheric pressure. In all three runs the pressure indicated on the test section and the peak pressures indicated by the film strip were approximately 600 p.s.i.

The next three runs were made with no expansion tank but a 250 c.c. nitrogen space in the reactor. A test section was on one of the 1" pipe outlets and a blowout disc on the other. In the first run a 1500 p.s.i. blowout disc was used. The equipment was fired and the blowout disc did not rupture. The test section and film strip both indicated a pressure of approximately 850 p.s.i. The second run was similar to the first except that the water was heated to 180°F. The blowout patch again did not rupture, and the test section and film strip both indicated approximately 950 p.s.i. For the third run a 120 p.s.i. blowout patch was used with water again at room temperature. This time the blowout patch ruptured. The highest peak pressure that was indicated by the film strip was too small to measure (less than 30 lbs.) while the test section indicated 1090 p.s.i.

The first six runs (above) of this series indicated that, if the effective pressure damage of the test piece, is plotted against the final static pressure, there was some optimum point of final static pressure where the least amount of damage would be done as indicated on the test section. (See Figure 14 and points denoted by subscript 1).

The last six runs of this section constituted an attempt to find that optimum point. The equipment was charged varying the nitrogen space in the expansion tank to give a variation in the final static pressure from 50 to 500 p.s.i. This series of runs did not give the evidence desired because of poor reproducibility of the reaction in respect to the test section. This reproducibility will be discussed later.

It is impossible to draw a definite conclusion from the data as presented; however, it does not rule out the possibility that the optimum point as presented earlier does not exist. The data is presented in graphic form in Figure 14, in which is plotted against the final static pressure, the effective pressure from the test piece and the actual peak static pressure as indicated on the film strip. The subscripts 1 and 2 indicate the runs made in the first and second sets of six runs each.

8. Third attempt to determine the effect of the pressure front created by the reaction. In the runs made in Series 6 where approximately 400 p.s.i. initial pressure was on the system, there were no noticeable irregularities called pressure front seen on the film strip. This series of runs was an investigation of the effect of initial pressure as to its ability to cut down or eliminate the pressure front damage. Three sets of runs have been made in the same equipment as Series 7. In each set the volume of the nitrogen space in the expansion tank was fixed while the initial pressure on the entire system was varied.

In the first set of runs the nitrogen space in the expansion tank was such as to give a 200 p.s.i. pressure rise for the complete reaction. The initial pressure was varied at 0, 50, 100, 200, 400, and 700 p.s.i. After the reactions were run a plot was made of the indicated test piece pressure and the actual peak static pressure from the film strip versus initial pressure (See Figure 15). The plot shows that if sufficient pressure is on the system the pressure front damage is eliminated. (A discussion as to the probable reason for this will follow later.)

The second set is a duplicate of the 50, 100, 200, and 400 p.s.i. initial pressure runs in the first set except that a relief valve was added to the system. The relief valve used was originally a 1000 p.s.i. hydraulic type in which the spring was changed in order that the relief setting might be approximately 50 p.s.i. above the initial pressure. This arrangement

worked very well at the higher pressures but at the 50 p.s.i. initial pressure run the relief valve blew down so far that it eliminated the effect of the initial pressure. The results of the four runs in this set have been plotted in Figure 16 where it can be noted the saving of 100 to 150 p.s.i. pressure in the 200 and 400 initial pressure runs.

In the third set of runs the nitrogen space was set to give a final pressure rise of 400 p.s.i. Runs were made with initial pressures of 0, 50, 100, 200, and 400 p.s.i. It was learned in Series 7 that a decrease in volume also had a tendency to curtail pressure front damage. The combination effect of initial pressure and the decrease in volume in the expansion tank show up in the plot (Figure 17), similar to that of the first set of runs, in that the effective test piece pressure did not go through a minimum.

ESTIMATED FINAL PRESSURES AND TEMPERATURES
OF SEVERAL REACTIONS AT CONSTANT VOLUME
IN A COMPLETELY FILLED CONTAINER

An estimation of the final pressures and temperatures at constant volume has been made and the results plotted (See Figure 22) for several reactions using 1 mol of sodium and varying the quantity of water present. For these calculations the physical properties of the products of the reaction were taken from the immediately available literature and are therefore subject to slight error. A possible error is also involved in extrapolating the values for the physical properties into the range of high temperatures and high pressures. The results of the calculations add much to the information collected to date on the reaction of NaK and liquid water.

In considering the reaction, there are a number of things that can effect the volume the hydrogen will occupy after completion. Four of the factors are listed below.

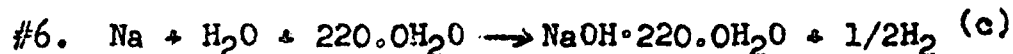
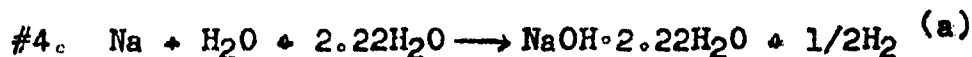
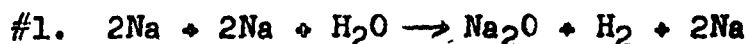
1. There is a reduction in volume in going from the non-gaseous reactants to the non-gaseous products of the reaction. This created volume is occupied by the generated hydrogen and fixes the maximum pressure that can ever be obtained due to the reaction.
2. If there is an excess of water or of sodium, an additional volume in which to confine the hydrogen is realized due to the compressibility of the reactant in excess.
3. In the calculations no additional volume was added for the expansion, due to pressure, of the container, nor was a reduction in volume considered due to the thermal expansion of the non-gaseous products of the reaction.

4. No consideration was given the solubility of hydrogen in either sodium or water.

The calculations were made assuming first, a completely adiabatic process and second, a completely isothermal process. This method gives the two extremes in the final pressure. Since in an actual reaction the container and surroundings will absorb part of the heat but not all of it, the final conditions must be somewhere between the points calculated.

In the reaction with, an excess of either sodium or H₂O in the adiabatic process, an instantaneous heat transfer rate has to be assumed for the excess material. An instantaneous heat transfer rate can not exist but neither is the reaction instantaneous.

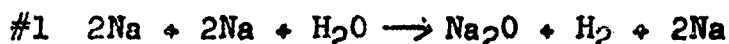
The chemical equations used for the calculations are



(a) to give a 50 Wgt. % solution of NaOH in H₂O.

(b) to give a 10 Wgt. % solution of NaOH in H₂O.

(c) to give a 1 Wgt. % solution of NaOH in H₂O.



Volume of 4Na = Wgt./sp.gr. (a) = $92/0.97 = 95.0$ cc

Volume of H₂O = $18/1 = 18.0$ cc

Total volume before reaction = 113.0 cc

(a) The values used for sp.gr. were taken from the Handbook of Chemistry and Physics. (3)

Volume of Na_2O $= 62/2.27 = 27.3 \text{ cc}$
 Volume of 2Na $= 46/0.97 = 47.5 \text{ cc}$
 Total volume of non-gaseous products $= 74.8 \text{ cc}$
 Remaining volume for the $\text{H}_2 = 113.0 - 74.8 = 38.2 \text{ cc}$

ISOTHERMAL REACTION

$$v = \frac{f}{p} \times \frac{V_0^{\circ} 1 \text{ atm}^{(b)}}{\text{M.W.}}$$

where v is the volume, f is the compressibility factor, P is the pressure, $V_0^{\circ} 1 \text{ atm}$ is the volume of gas at 1 atm, and M.W. is the molecular weight.

$$38.2 = \frac{f}{p} \times \frac{22.428}{2.0154}, \quad \frac{f}{p} = .00343$$

From the table of compressibility for H_2 a value of $\frac{f}{p} = .00343$ gives

$$P = 5,800 \text{ p.s.i.}$$

ADIABATIC REACTION

The heat given up by the reaction is obtained by the difference in the heats of formation^(c) of the compounds in equation # 1

$$Q = 99,450 - 68,320 = 31,130 \text{ cal.}$$

For the Q calculated, the H_2 was at atmospheric pressure. It is assumed that the energy required to compress the gas is equal to the energy gain, and the only addition necessary is the work in expanding against the atmosphere.

$$\text{work} = P \frac{V_2 - V_1}{J} = \frac{980 \times 22,428}{1000 \times 41.3} = 523 \text{ cal}$$

then the total heat of the reaction is $31,130 + 523 = 31,653 \text{ cal.}$

- (b) The equation for the compressibility of gases and the values used for H_2 were taken from Chemical Engineers Handbook.⁽⁴⁾
- (c) The heats of formation were taken from Hougen and Watson, Chemical Process Principles.⁽⁵⁾

In the adiabatic process all the heat of the reaction must go into the products of the reaction only. Plots for the total heat content have been prepared for Na, (a) Na₂O, (b) and H₂ (c). These plots are presented in Figures 17, 18, and 19.

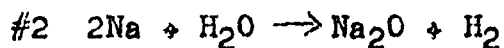
Assuming a temperature of 1080°K the total heat distribution in the Na, Na₂O, and H₂ from the total heat curves is.

$$12,400 + 4000 + 15,200 = 31,600 \text{ while } q = 31,653$$

$$\text{Then } T = 1080^{\circ}\text{K or } 1483^{\circ}\text{F}$$

Since hydrogen at high pressure tends to behave more and more like an ideal gas with increased temperature it is assumed that the perfect gas laws can be used to find the final pressure.

$$P_2 = \frac{P_1 V_1 \times T_2}{T_1 \times V_2} = \frac{14.7 \times 22,800 \times 1080}{291 \times 38.2} = 32,400 \text{ p.s.i.}$$



$$\text{Volume of } 2\text{Na} = 46/0.97 = 47.5 \text{ cc}$$

$$\text{Volume of } \text{H}_2\text{O} = 18/1 = 18.0 \text{ cc}$$

$$\text{Total volume before reaction} = 65.5 \text{ cc}$$

$$\text{Volume of } \text{Na}_2\text{O} = 27.3 \text{ cc}$$

$$\text{Remaining volume for the } \text{H}_2 = 65.5 - 27.3 = 38.2 \text{ cc}$$

ISOTHERMAL REACTION

Since the volume and quantity of H₂ is the same as in equation # 1

$$P = 5,800 \text{ p.s.i.}$$

-
- (a) The data for Na, Figure 17, were calculated from Ginnings, Douglas, and Ball's report. (6)
 - (b) The total heat curve for Na₂O in Figure 18 was prepared by calculating the data presented by Naylor. (7)
 - (c) The total heat curve, Figure 19, was calculated from the sp.ht. equation for H₂ given in Getman and Danials Textbook. (8)

ADIABATIC REACTION

The total heat, including the work factor, is again the same as calculated for equation # 1 or 31,653 cal.

The heat must go into the Na₂O and the H₂. Figures 18 and 19 give the total heat curve for Na₂O and H₂.

Assuming a temperature of 1258°K

then 26,653 + 5000 = 31,653 cal.

T = 1258 K or 1772°F

Assuming an ideal gas

$$P_2 = \frac{14.7 \times 22,800 \times 1258}{291 \times 38.2} = 37,800 \text{ p.s.i.}$$



Volume of Na = 23/0.97 = 23.7 cc

Volume of H₂O = 18/1 = 18.0 cc

Total volume before reaction = 41.7 cc

Volume of NaOH = 40/2.13 = 18.76 cc

Remaining volume for the H₂ = 47.1 - 18.76 = 22.94 cc

ISOTHERMAL REACTION

$$v = \frac{f}{p} \times \frac{V_0^{\circ} 1 \text{ atm}}{\text{M.W.}}$$

$$22.96 = \frac{f}{p} \times \frac{11,214}{2.0154}, \quad \frac{f}{p} = .00410$$

From the table for the compressibility of H₂ a value of $\frac{f}{p}$ = .00410 gives

P = 4,700 p.s.i.

ADIABATIC REACTION

The heat of the reaction at atmospheric pressure is

Q = 101,960 - 68,320 = 33,640 cal

$$\text{expansion work} = \frac{P(V_2 - V_1)}{J} = \frac{11,214 \times 980}{1000 \times 41.3} = 266$$

$$\text{total heat} = 33,640 + 266 = 33,906.$$

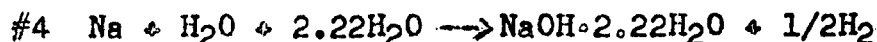
The heat must go in the H_2 and $NaOH$, Figure 19 and 20 give the total heat curves for $NaOH(a)$ and H_2 .

Assuming a temperature of $1700^\circ K$ the total heats are $30,000 + 1/2 \times 7,600 = 33,800$ cal while $q = 33,906$.

$$\text{Temperature} = 1700^\circ K \text{ or } 2,600^\circ F$$

Assuming an ideal gas

$$P_2 = \frac{14.7 \times 11,400 \times 1700}{291 \times 22.96} = 43,700 \text{ p.s.i.}$$



$$\text{Volume of Na} = 23/0.97 = 23.7 \text{ cc}$$

$$\text{Volume of } 3.22H_2O = 58/0.97 = 58.0 \text{ cc}$$

Total volume before reaction

$$\text{Volume of } NaOH \cdot 2.22H_2O = \frac{80}{1.525} = 54.4 \text{ cc}$$

$$\text{Volume for the } H_2 = 81.7 - 54.4 = 29.3 \text{ cc}$$

ISOTHERMAL REACTION

$$v = \frac{f}{p} \times \frac{V_0^\circ 1 \text{ atm}}{M.W.}$$

$$29.3 = \frac{f}{p} \times \frac{11,214}{2.0154}, \quad \frac{f}{p} = .00525$$

From the table for H_2 at $\frac{f}{p} = .00525$, $P = 3530$ p.s.i.

ADIABATIC REACTION

With the addition of the heat of solution^(b) to the heat of formation

$$Q = 101,960 - 68,320 + 5000 = 38,640 \text{ cal}$$

- (a) The total heat curve, Figure 20, assuming the sp.ht. reported by Terashkovich and Vismorskie is constant for all temperatures⁽⁹⁾. The heat of transition and heat of fusion reported by von Heresy is also included⁽¹⁰⁾.
- (b) Data taken from Hogen and Watson Textbook⁽⁵⁾.

work energy as before = 266 cal

Total heat $q = 38,640 + 266 = 38,906$

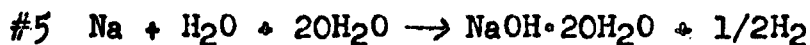
Assuming the sp.ht. of 50% aqueous solution of NaOH to be .764(a).

Assume a temperature of 911°K

then $610 \times 764 \times 80 + 1/2 \ 3100 = 38,850$ cal

Temperature = 911°K or 1180°F

$$P_2 = \frac{14.7 \times 11,214 \times 911}{291 \times 29.3} = \underline{17,400 \text{ p.s.i.}}$$



Volume of Na = $23/0.97 = 23.7$ cc

Volume of $21\text{H}_2\text{O} = 378/0.97 = \underline{378.0}$ cc

Total volume before reaction = 401.7 cc

Volume of $\text{NaOH} \cdot 2\text{OH}_2\text{O} = \frac{400}{1.109} = 360.7$ cc

Remaining volume for the $\text{H}_2\text{O} = 401.7 - 360.7 = 41.0$ cc

ISOTHERMAL REACTION

Assuming only the H_2O in the NaOH is compressible and assuming a pressure of 170 atm. the compressibility factor is $1.0015 - .9942 = .0073$ (b).

The additional volume = $.0073 \times 360 = 2.62$ cc

$$v = \frac{f}{p} \times \frac{V_0^0 \ 1 \text{ atm.}}{\text{M.W.}}$$

$$41.0 + 2.62 = \frac{f}{p} \times \frac{11,214}{2.0154}, \quad \frac{f}{p} = .00782$$

The pressure represented by an $\frac{f}{p}$ of .00782 is

$P = 167$ atm. or $2,460$ p.s.i.

(a) Data taken from Bertelli and McCabe(11).

(b) Compressibility of water taken from Mechanical Engineers Handbook(12).

ADIABATIC REACTION

The total heat of the reaction including work is

$$Q = 101,960 - 68,320 + 10,300 + 266 = 44,206 \text{ cal}$$

Assuming the sp.ht. of $\text{NaOH} \cdot 20\text{H}_2\text{O}$ to be .923^(a) and assuming a temperature of 410°K , then

$$400 \times .923 \times 119 + 1/2 \times 550 = 44,275 \text{ cal}$$

Assuming 210 atm. final pressure the compressibility factor for the water is $1.0015 - .993 = .0085$.

The additional volume is $.0085 \times 360 = 3.06 \text{ cc}$

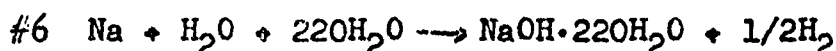
$$v = \frac{f}{p} \times \frac{V_0 \circ 1 \text{ atm}}{M.W.}$$

$$41.0 + 3.06 = \frac{f}{c} \times \frac{11,214}{2.0154}, \quad \frac{f}{c} = .00773$$

$$P = 137^\circ\text{C} \text{ and } \frac{f}{c} \text{ of } .00773 = 219 \text{ atm}$$

$$P = 3,220 \text{ p.s.i.}$$

$$T = 278^\circ\text{F}$$



$$\text{Volume of Na} = 23/0.97 = 23.7 \text{ cc}$$

$$\text{Volume of } 221 \text{ H}_2\text{O} = 3978/1 = 3978.0 \text{ cc}$$

$$\text{Total volume before reaction} = 4001.7 \text{ cc}$$

$$\text{Volume of NaOH } 220 \text{ H}_2\text{O} = \frac{4000}{1.0095} = 3961.2 \text{ cc}$$

$$\text{Remaining volume for H}_2 = 4001.7 - 3961.2 = 40.5 \text{ cc}$$

ISOTHERMAL REACTION

$$\text{Assuming } 110 \text{ atm } \Delta v = 1.0015 - .9965 = .0050$$

$$\text{The additional volume} = 3960 \times .0050 = 19.8$$

(a) Data taken from Bertelli and McCabe⁽¹¹⁾.

$$v = \frac{f}{p} \times \frac{V_0^0 \text{ 1 atm}}{\text{M.W.}}$$

$$40.5 + 19.8 = \frac{f}{p} \times \frac{11.214}{2.0154}, \quad \frac{f}{p} = .0182$$

$$P = 110.5 \text{ atm or } \underline{1627 \text{ p.s.i.}}$$

ADIABATIC REACTION

The total heat of the reaction including work is

$$q = 101,960 - 68,320 + 10,120 - 266 = 44,020 \text{ cal}$$

Assuming the sp.ht. of $\text{NaOH} \cdot 22\text{OH}_2\text{O}$ to be .985 and assuming a temperature of 302°K

$$\text{then } 4000 \times .985 \times 11 + 1/2 \text{ 250} = 43,525 \text{ cal}$$

$$T = 302^\circ\text{K or } \underline{84^\circ\text{F}}$$

Assuming 110 atm final pressure the compressibility factor for water is $1.0015 - .9965 = .0050$

$$\text{Additional volume} = 3960 \times .0050 = 19.8$$

$$P \text{ at } \frac{f}{p} \text{ of } .0182 \text{ and } 84^\circ\text{F} = 113 \text{ atm}$$

$$P = 1660 \text{ p.s.i.}$$

The above calculations are for complete reaction assuming that all the product heat goes into the NaOH or Na_2O and the H_2 . This is the extreme case above which higher pressures and temperatures are impossible. However, in any reaction the heat cannot be isolated from its surroundings and with sufficient time the entire system must come to equal temperature.

DISCUSSION

The fact that the reaction is not reproducible has been of great concern, and until recently no satisfactory theory as to the nature of the reaction could be given that would explain the wide differences in results obtained in the 71 runs made to date. However, in light of the information obtained in Series 7 and 8, a supposition has been made as to the actual mixing and reacting of the NaK and the water during any run.

It has been shown in Series 6 that the non-reproducibility of the reaction is not in the trigger mechanism and so therefore must be in the reaction itself.

Series 7 gives a method of separating the effect of pressure front and static pressure build-up. It was noted in Series 7 that in the runs where the pressure front damage was in excess to that of static pressure build-up there was always two or more sets of irregularities on the film pressure trace. Also it was noted that in the same runs the subsequent marks were always greater than the marks designating the opening of the plunger.

This fact is evident in Figure 8 where the slight disturbance of the trigger opening can be seen on the right hand side of the upper trace while the greatest disturbance is some three cycles downfilm (this time of 3 cycles is not necessarily representative of all the runs since sometimes the time between the first and second pulse is as much as 20 cycles).

When the plunger is pulled back from the seat, it creates an instantaneous void space that must be replaced by the water. This water can enter from any one or all points around the entire diameter of the seat. If the water enters slightly faster from one side than from the other, the reaction would take place first from that side. When the water and the NaK make contact a hydrogen bubble is formed which displaces a small quantity of NaK that will be swept out of the NaK chamber into the surrounding water. This small quantity of free NaK will react rapidly with the water, thereby creating an instantaneous pressure or pressure front, (the second set of irregular marks on the film). The remaining NaK and water which is constantly being separated by the hydrogen will again go through the same process until such time as the water entering and the hydrogen given up by the reaction will reach an equilibrium at which time the pressure rise will follow in a steady state.

The preceding supposition is substantiated by two facts: (1) that in the runs where an initial pressure was on the system the gas bubble generated would necessarily be smaller and the sweeping effect not as great, thereby eliminating the high pressure front vibrations; (2) that in the test where the 1" pipe nipple was thrown into the pond there was a sharp report followed by a steady stream of small bubbles coming up to the surface of the pond.

It has been shown until the time of complete reaction in the tests presented, that the reactants are continuously being separated by the H_2 that is given up, thus increasing the total reaction time. It has also been shown in Section 1 that the final temperature and pressure of the reaction can be predicted assuming the heat of the reactor is distributed equally among the products of the reaction and the surroundings. However, any intermediate step in the reaction is unpredictable. It is not known at any instant how much of the products have reacted or how much heat goes into the gas that has reacted;

consequently, the instantaneous volume or pressure is unknown. The retention of all the heat of the reactions only by the products of the reaction is impossible and does not occur, but a part of the heat can and does remain in the gas, and for an instant a tremendous surge of pressure is generated which will show up as a pressure front and also start the movement of the surrounding liquid away from the point of reaction. It is unfortunate then that the water and NaK cannot maintain contact, and for this reason the total time of the complete reaction is increased thus allowing more time for the heat of the reaction to be dissipated into the surrounding materials.

Other investigators in the field have encountered the same problem as presented here, the poor reproducibility of the reaction in relation to the phenomenon referred to in this report as pressure front. The Naval Research Laboratory reported⁽¹³⁾ peak pressures in some instances nearly 100% greater than the final equilibrium values. Kilpatrick⁽¹⁴⁾ reports two definite stages to the reaction with a pressure rise far in excess to the expected pressure; he also reports the second rise larger than the first.

Both NRL and Kilpatrick attribute part of the high peak pressures obtained to vapor pressure of the surrounding water in that the heat of the reaction has, at the instant, not sufficient time to be dissipated to the surrounding material. This fact may be true, however, it is the opinion of the authors of this paper that due to the extremely high pressure existing in the pressure front, vaporization to any noticeable extent will not take place and the peak is a result of the instantaneous high heat content of the hydrogen gas.

CONCLUSIONS

It can be stated that the reaction of NaK and superheated steam is of little danger to equipment or personnel and that the reaction liberates a smaller volume of hydrogen than that which was originally occupied by the steam. This fact has been presented in a previous report⁽¹⁾ and has also been discussed under Series I under this report. The steam-NaK reaction can be summarized by the statement that should a break occur in the superheater the resulting pressure on the entire system cannot exceed the pressure of the steam entering the chamber. This conclusion assumes the NaK does not flow back through the steam pipes into the separator or any place it might find liquid water.

Two conclusions can thus far be drawn for the reaction between NaK and liquid water:

1. The reaction of NaK and liquid water is impeded by the continual separation of the two reactants by the generated hydrogen. This separation of the two reactants increases the time required for a total reaction and makes it possible to relieve the pressures generated through prepared piping.
2. By means of the initial pressure on the system the pressure front created by the reaction can be controlled, making it possible to design equipment only to withstand the pressure generated by the complete reaction.

FUTURE WORK

This paper cannot at this time set down hard and fast safety rules for the design of exchangers using NaK and water. More work is necessary before definite recommendations can be made. The plans for the future work are:

1. In the immediate future it is planned to make more runs in the present equipment described in Series 8 in which both initial pressure and volume will be varied.
2. Study should be made of the reaction at elevated temperatures.
3. It would be advisable to set up a system in which both streams are flowing, that is, simulating a heat exchanger in operation. This system should include shutoff valves and relief piping.
4. It is hoped that the pressure measuring equipment can be modified for the use of strain gauges in order to obtain a linear pressure response.
5. A more fundamental study of the reaction could be made with high speed motion pictures.
6. A reactor with completely filled chambers and no nitrogen space might be of value in checking the theoretical calculations.

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13. Letter report excerpted from NRL Report C-3508 which is in the process of publication.
14. Kilpatrick, Martin, "Research on Liquid Fuels" Annual Report, September 14, 1949.

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FIGURE-1

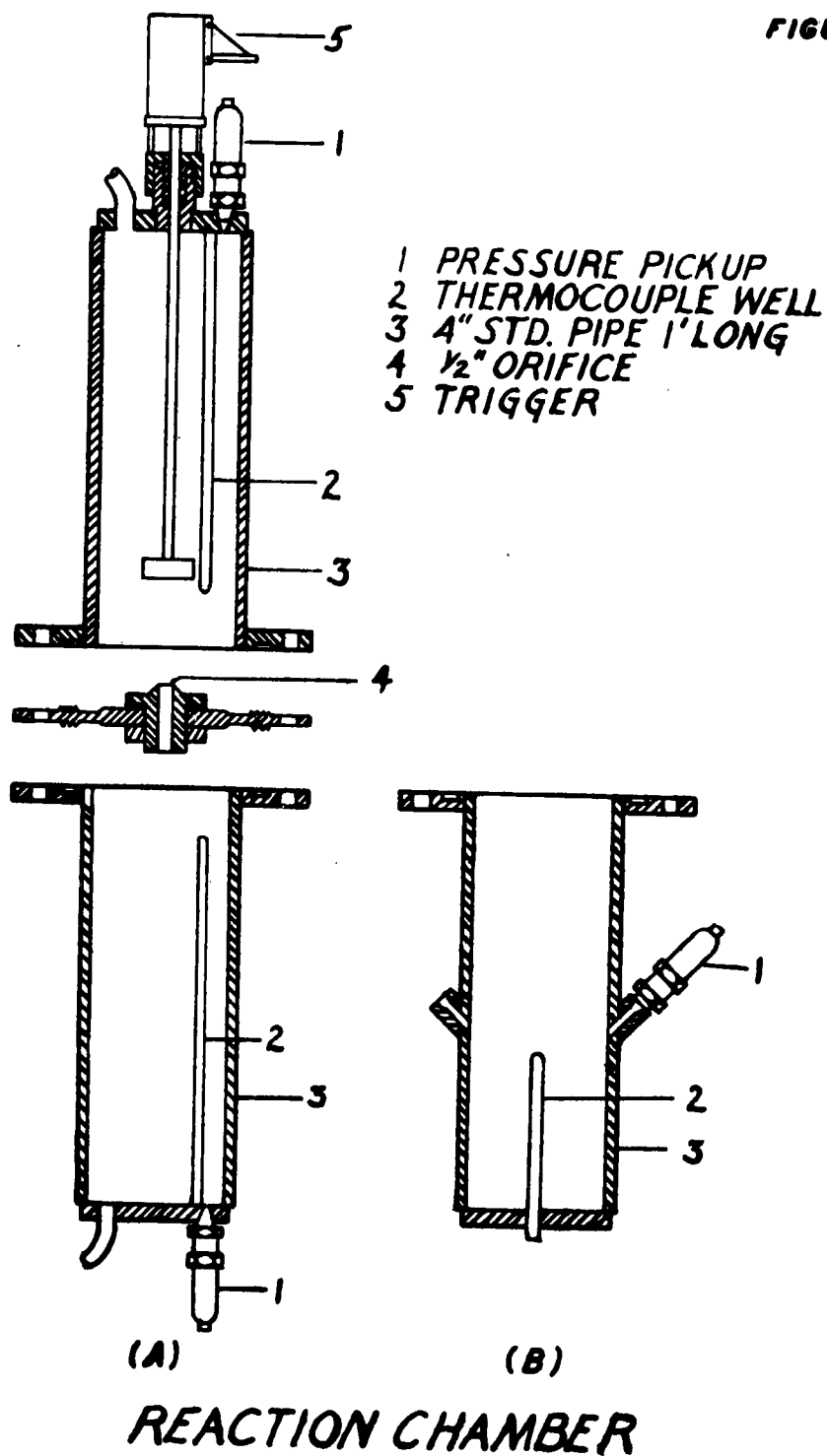
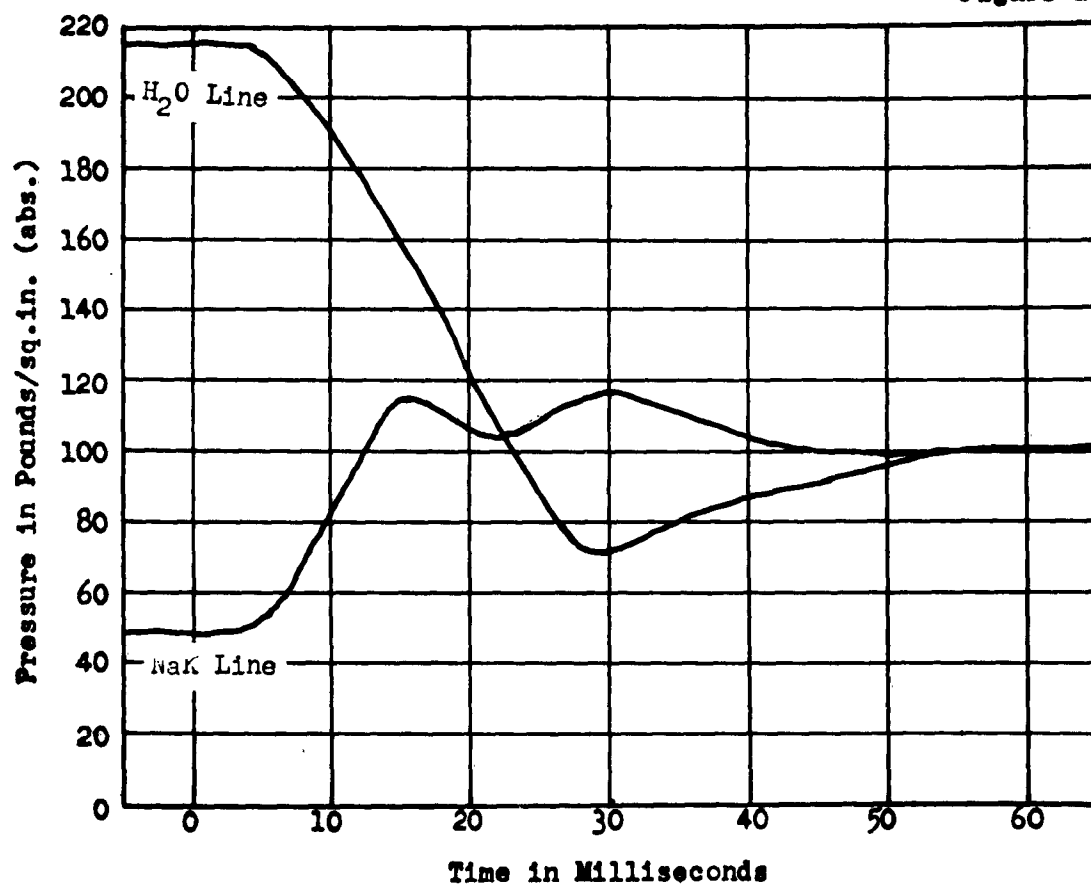
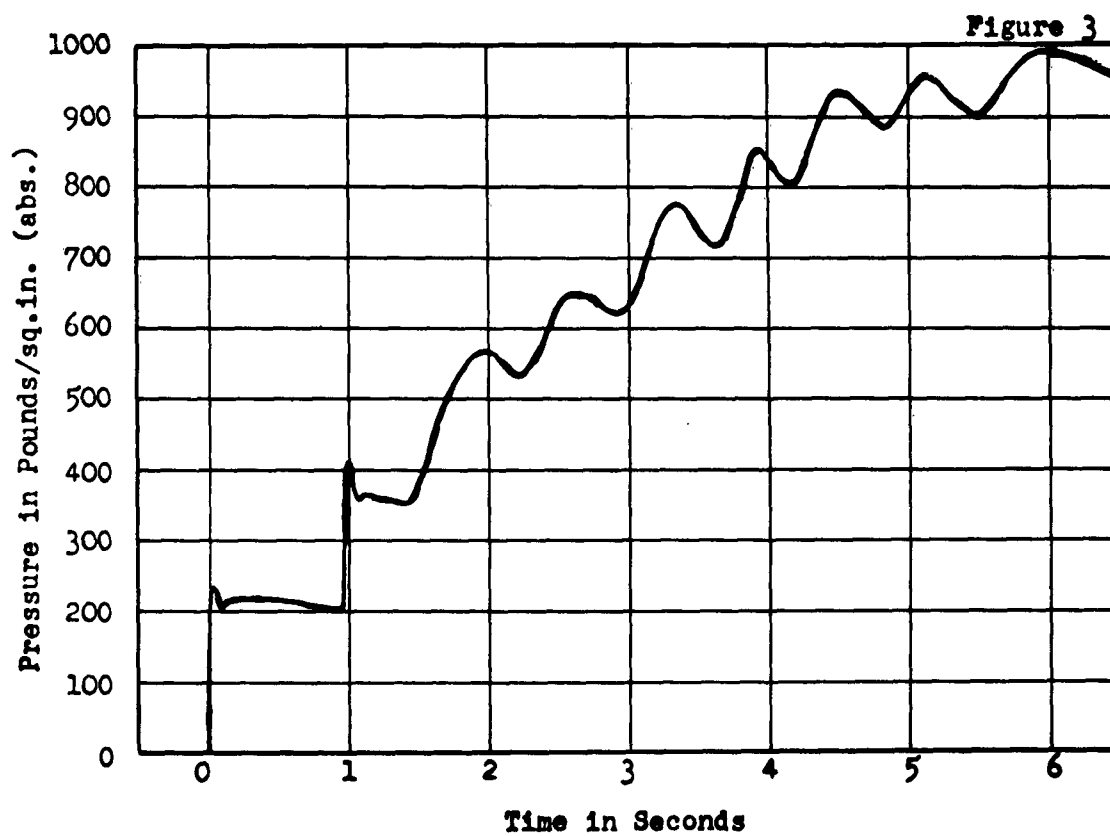


Figure 2

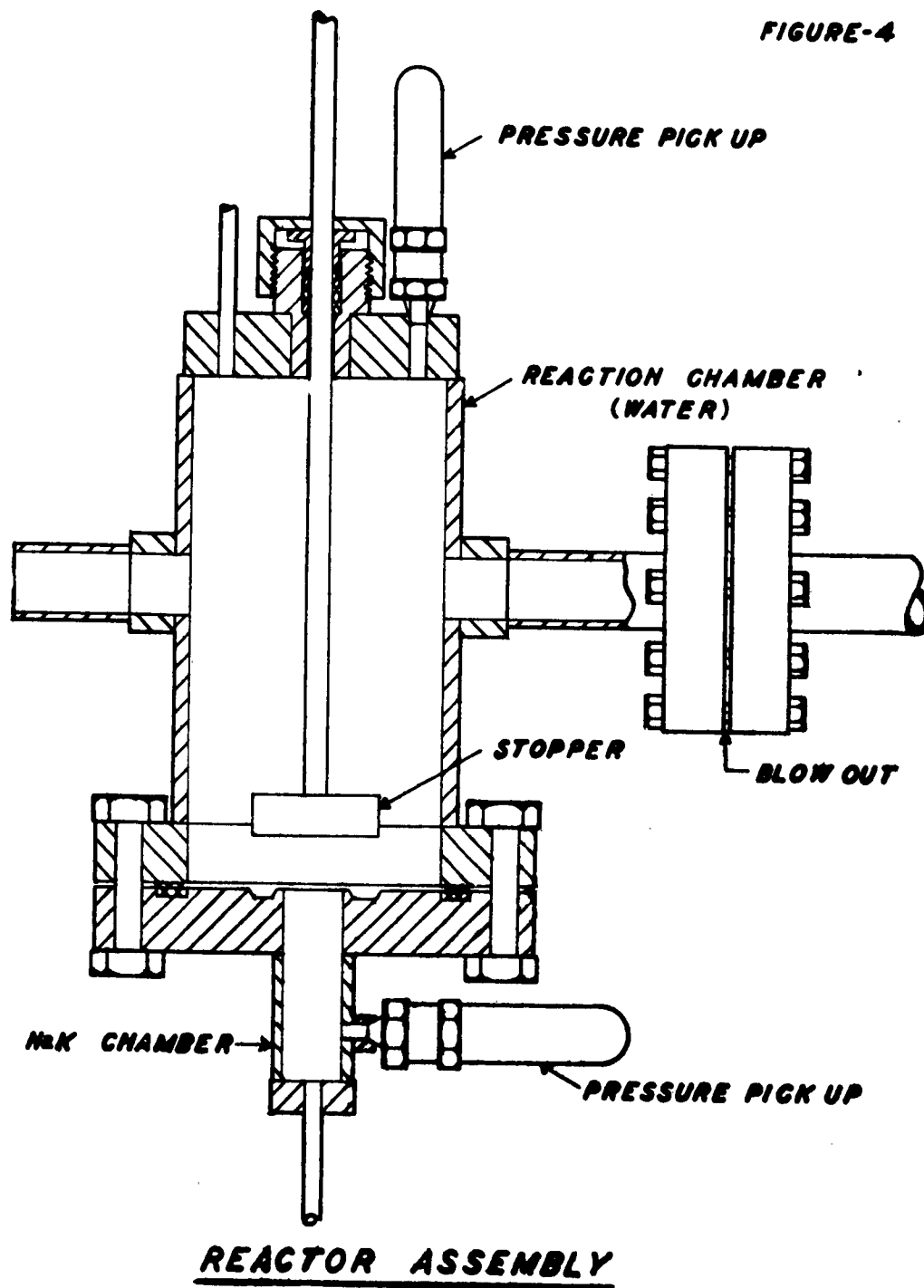


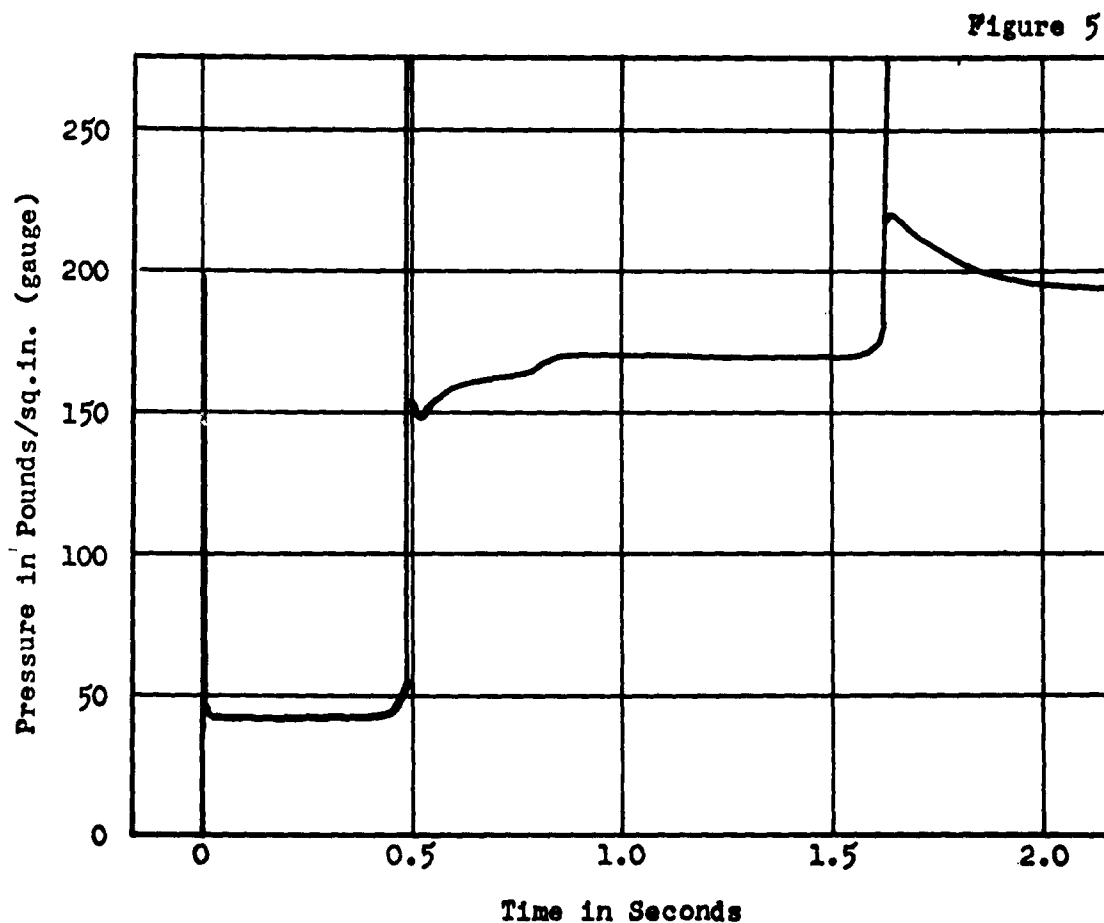
PRESSURE-TIME RELATIONSHIP FOR THE THIRD STEAM RUN USING 200 P.S.I.(G)
15°F SUPERHEAT STEAM AND 2½ POUNDS OF NAK.



PRESSURE-TIME RELATIONSHIP FOR THE THIRD RUN OF THE FIRST SERIES OF WATER RUNS USING $2\frac{1}{2}$ POUNDS OF NAK AND 200 CC OF WATER.

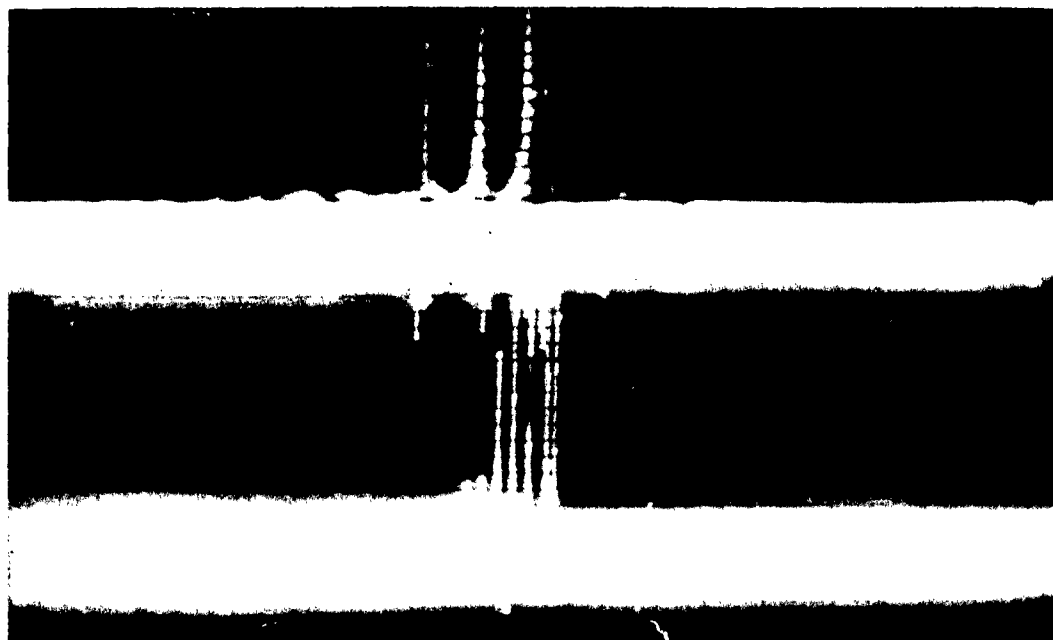
FIGURE-4





PRESSURE-TIME RELATIONSHIP FOR THE FIRST RUN IN THE SECOND
SERIES OF WATER RUNS USING AN EXCESS OF WATER, 49 CC OF NAK,
AND WITH A 1000 CC NITROGEN SPACE.

Figure 6



REPRODUCTION OF THE SECTION OF THE FILM STRIP
SHOWING THE PRESSURE FRONT CREATED BY THE FIRST REACTION
OF RUN 3-4.

Time goes from right to left.

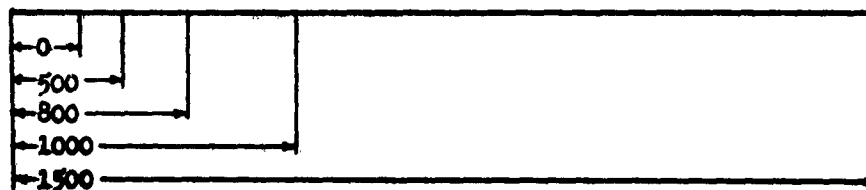
Upper trace represents pressure in H_2O chamber.

Lower trace represents pressure in NaK chamber.

Evenly spaced pips in upper trace are 1/60 second
apart in time.

Trace width represents pounds/sq.in.

Approximate Scale



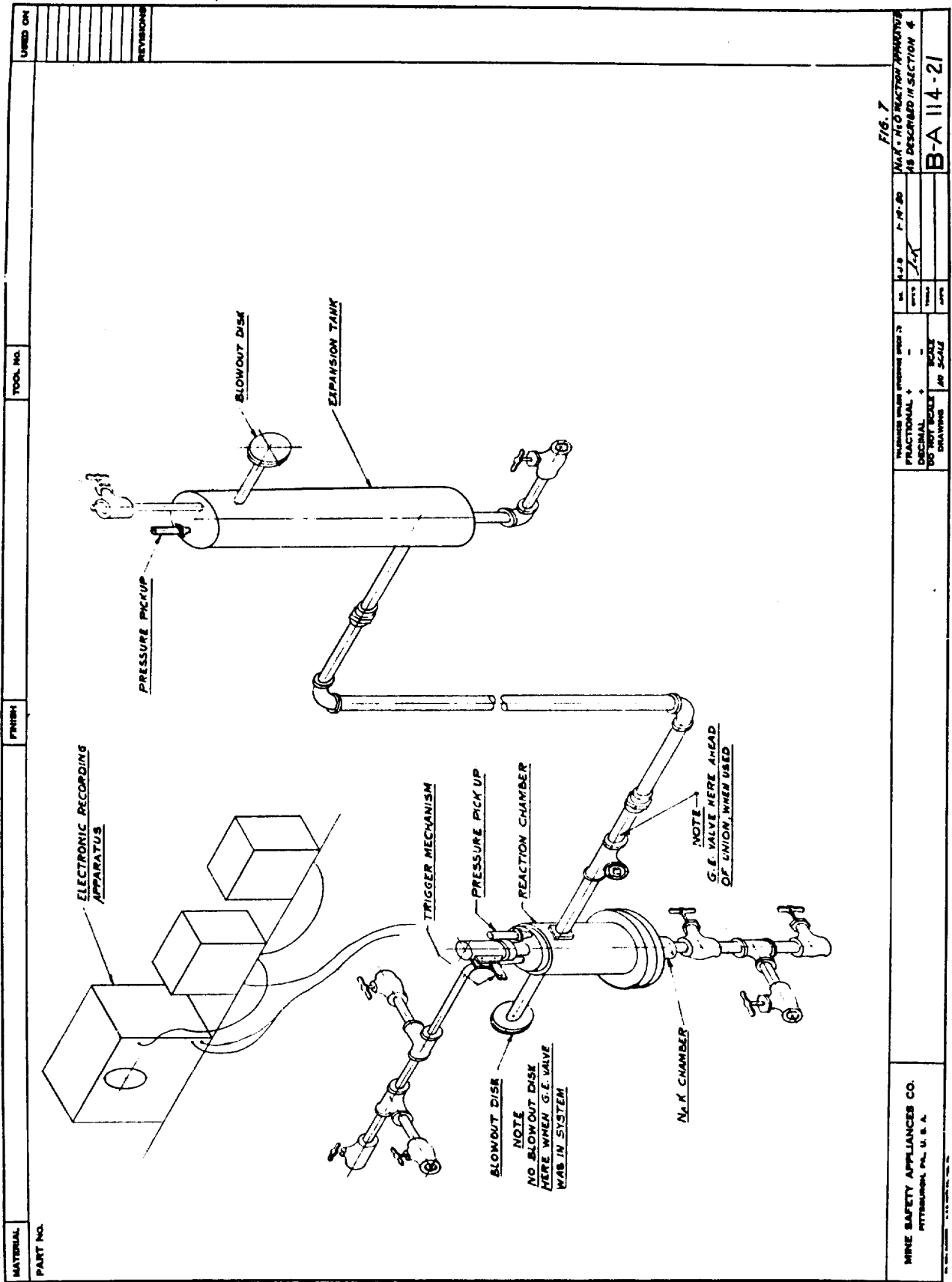
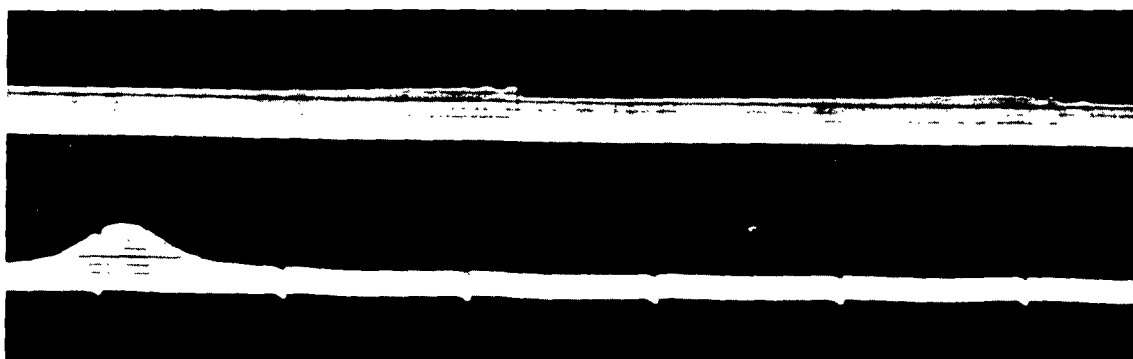


FIG. 7

MINE SAFETY APPLIANCES CO. PITTSBURGH, PA. U. S. A.		N.A.K. - N ₂ O REACTION APPARATUS AS DESCRIBED IN SECTION 4	
PART NO.		B-A 114-21	
MATERIAL		N.A.K.	
FINISH		N.A.K.	
TOOL NO.		N.A.K.	
USED ON		N.A.K.	
REVISIONS		N.A.K.	
UNION		N.A.K.	
FRACTIONAL		N.A.K.	
DECIMAL		N.A.K.	
DO NOT SCALE		N.A.K.	
SCALE		N.A.K.	
DRAWING		N.A.K.	

Figure 8



SECTION OF THE FILM STRIP FROM THE
SECOND RUN OF THE SECOND SERIES AS DESCRIBED
IN SECTION 4.

Time goes from right to left.

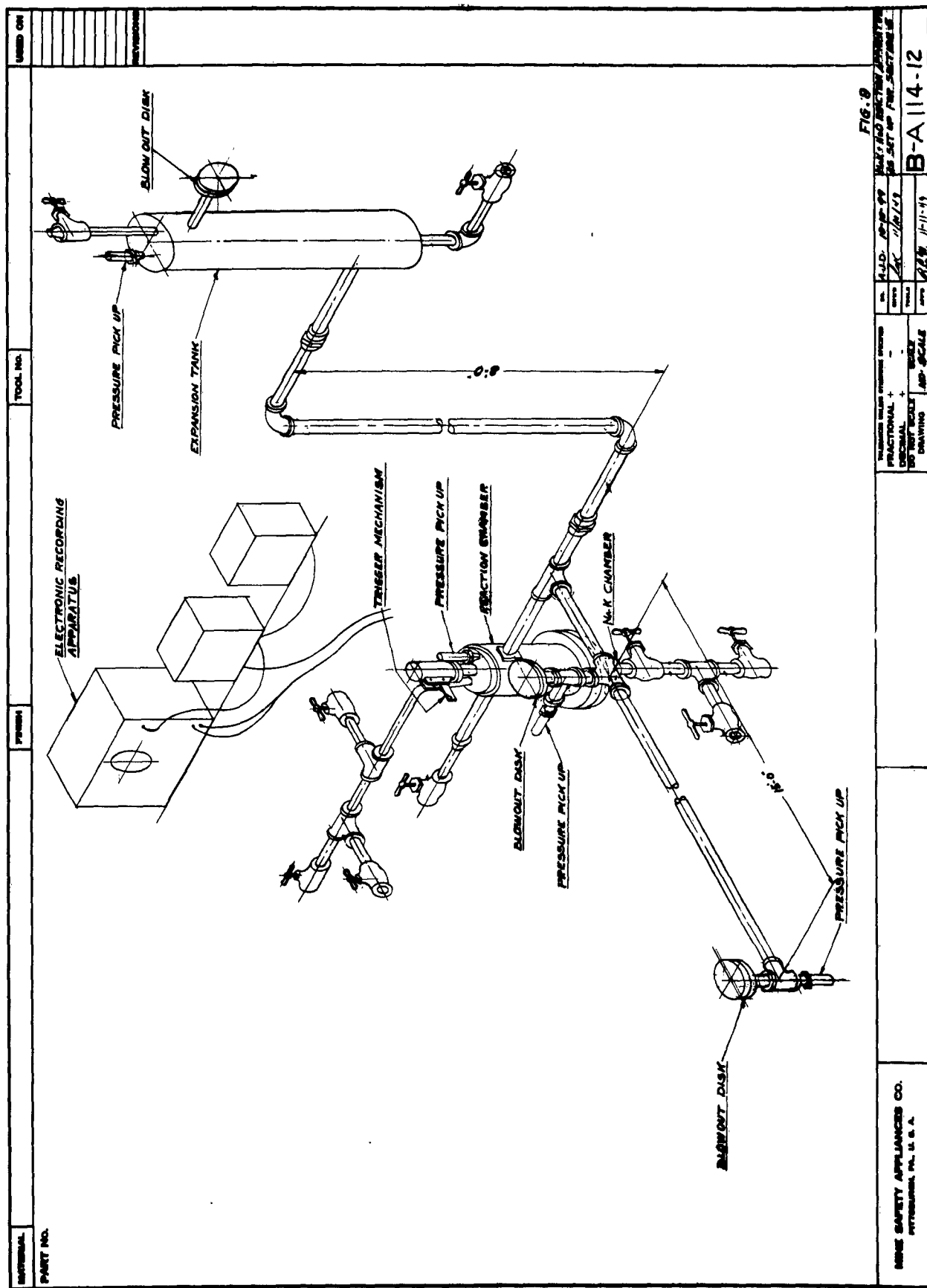
The upper trace represents the pressure in the reactor.

The lower trace represents the pressure in the expansion tank.

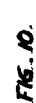
The highest peak shown in the reactor is 550 p.s.i.

The highest peak in the expansion tank is 780 p.s.i.

The regular pips occurring in the lower trace are time marks representing $1/60$ second.



MATERIAL		PART NO.		FORM		TOOL NO.		USED ON	
MINE SAFETY APPLIANCES CO.		PITTSBURGH, PA. U. S. A.							
DRAWING		MP-SCALE		PROJECT		NO. 4-10-10-10-10		DATE 11/11/53	
FRACTIONAL +		ORIGINAL		REVISION		BY		DATE	
B-A114-12									



Na,K-H₂O REACTION APPARATUS
FOR SECTION 4

MINI SAFETY APPLIANCE CO.

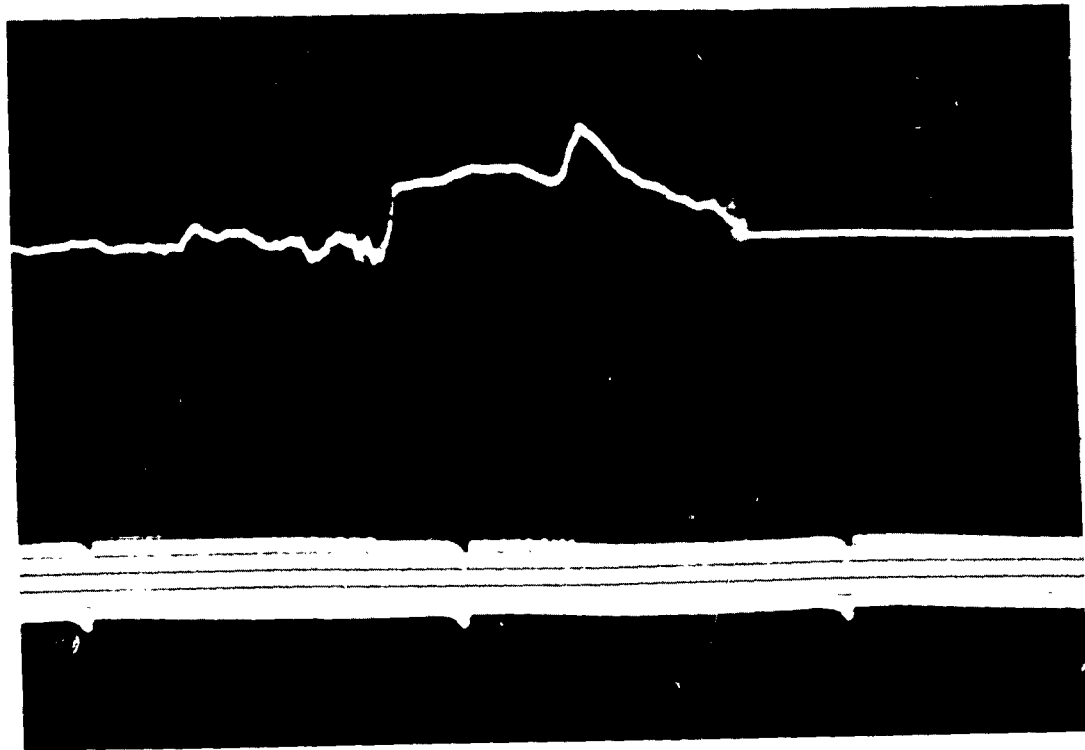
SAFETY APPLIANCE
PITTSBURGH, PA., U.S.A.

SECRET

11-14-11

6/1/69

Figure 11



SECTION OF FILM STRIP SHOWING
TRIGGER TRACE AS DESCRIBED IN SECTION 6

Time moves from right to left.

Time marks at 1/60 second intervals.

MATERIAL	FINISH	TOOL NO.	USED ON
PART NO.			
<p>FIG. 12</p> <p>SECTION AA</p>			
MINE SAFETY APPLIANCES CO. PITTSBURGH, PA. U. S. A.		DR. A.J.D. 10-10-49 CH'D J.K. 11/11/49 TOLLS APP'D R.B.W. 11-11-49	
TOLERANCES UNLESS OTHERWISE SPECIFIED FRACTIONAL + DECIMAL - DO NOT SCALE DRAWING		PRESSURE TEST SECTION C-A 114-7	

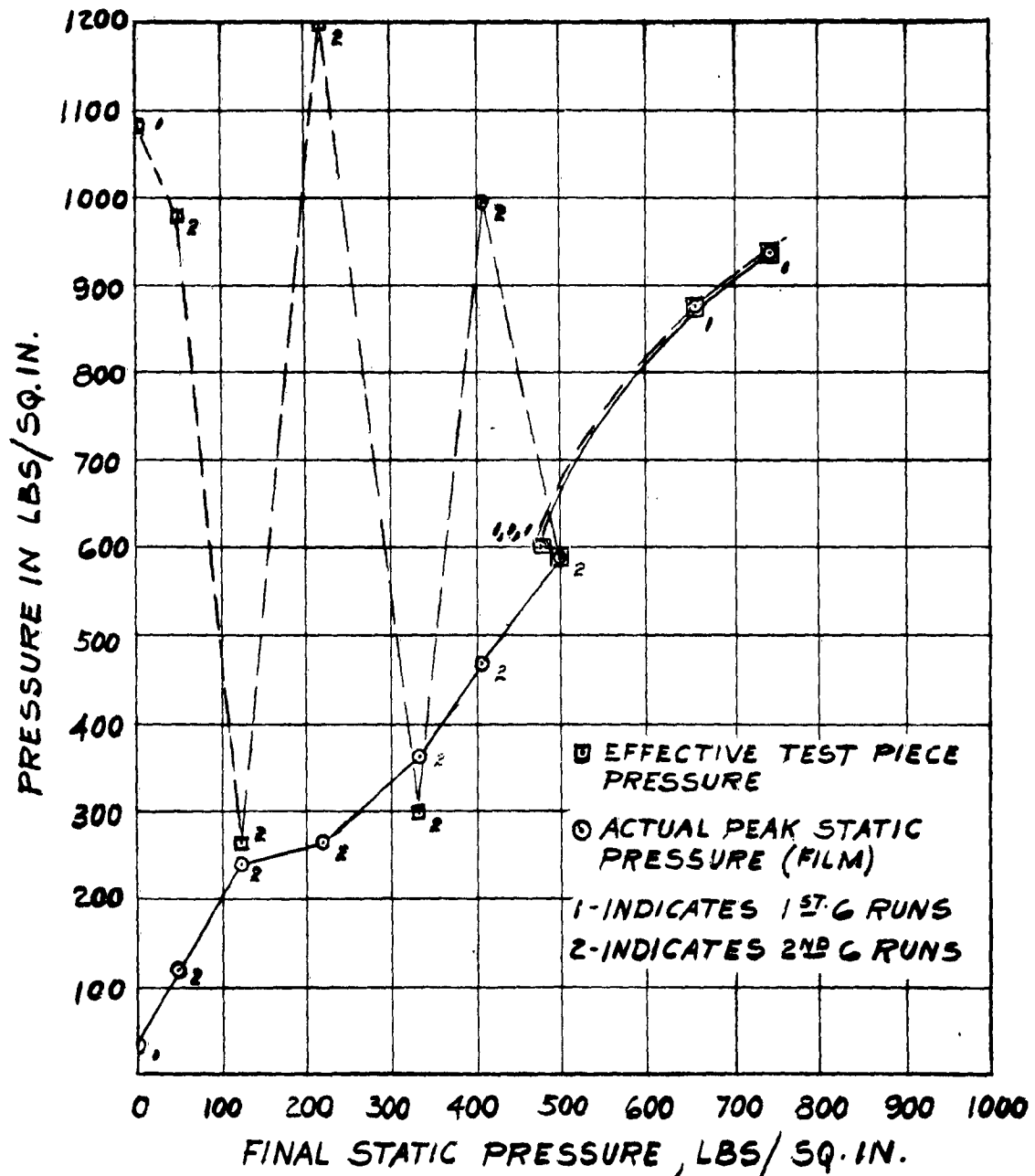


FIG 14. PLOT OF THE EFFECTIVE TEST PIECE PRESSURE AND THE ACTUAL PEAK STATIC PRESSURE (FROM THE FILM STRIP) V.S. THE FINAL STATIC PRESSURE. ALL RUNS MADE AT 0 P.S.I. INITIAL PRESSURE

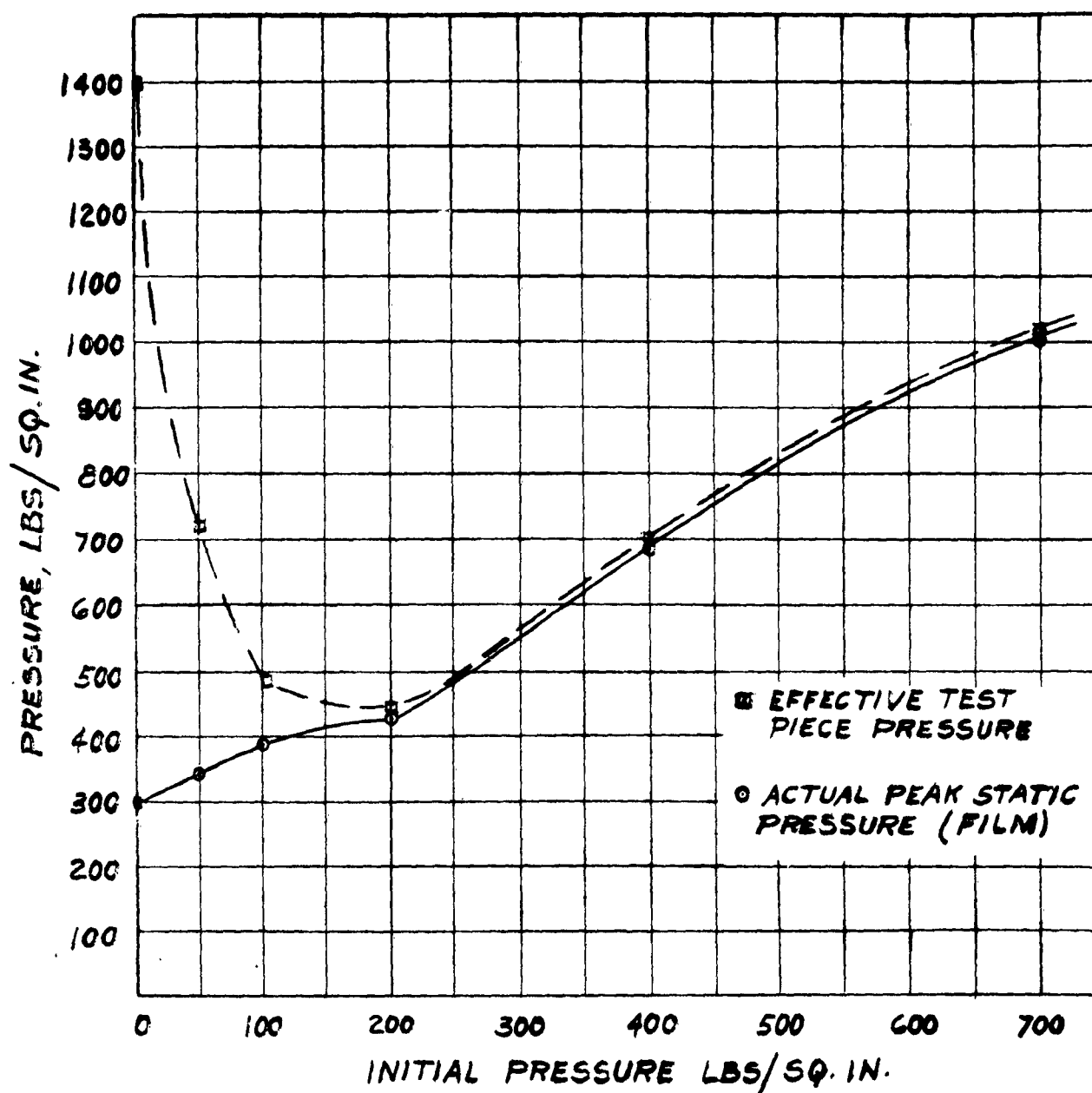


FIG. 15 PLOT OF THE EFFECTIVE TEST PIECE PRESSURE AND THE ACTUAL PEAK STATIC PRESSURE (FROM FILM STRIP) V.S. THE INITIAL PRESSURE. ALL RUNS SET TO GIVE A FINAL PRESSURE RISE OF 200 p.s.i.

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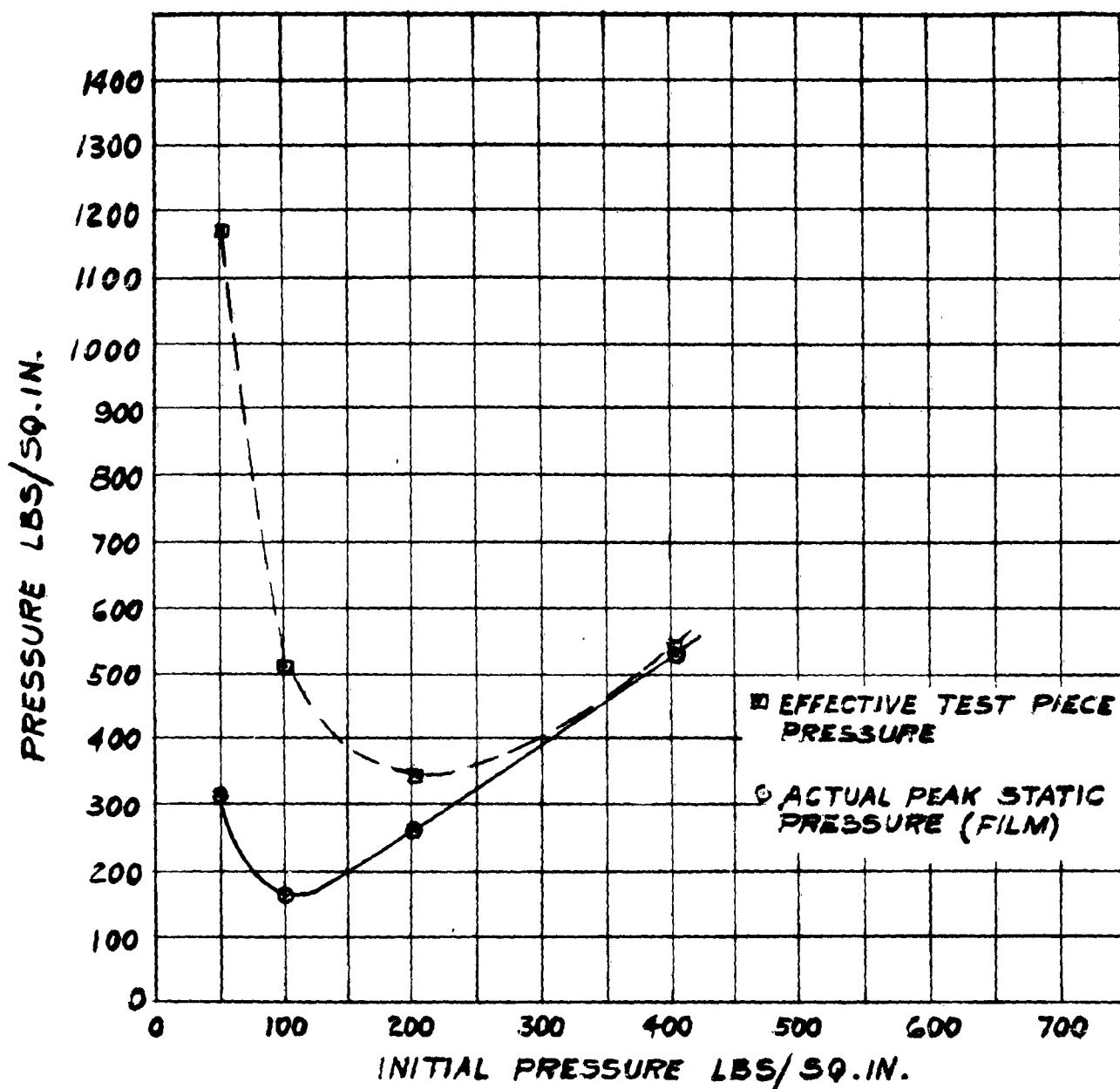


FIG. 16 PLOT OF THE EFFECTIVE TEST PIECE PRESSURE AND THE ACTUAL PEAK STATIC PRESSURE (FROM FILM STRIP) V.S. THE INITIAL PRESSURE. N_2 SPACE WOULD GIVE 200 p.s.i. PRESSURE RISE. RELIEF VALVE SET AT 50 p.s.i. ABOVE INITIAL PRESSURE

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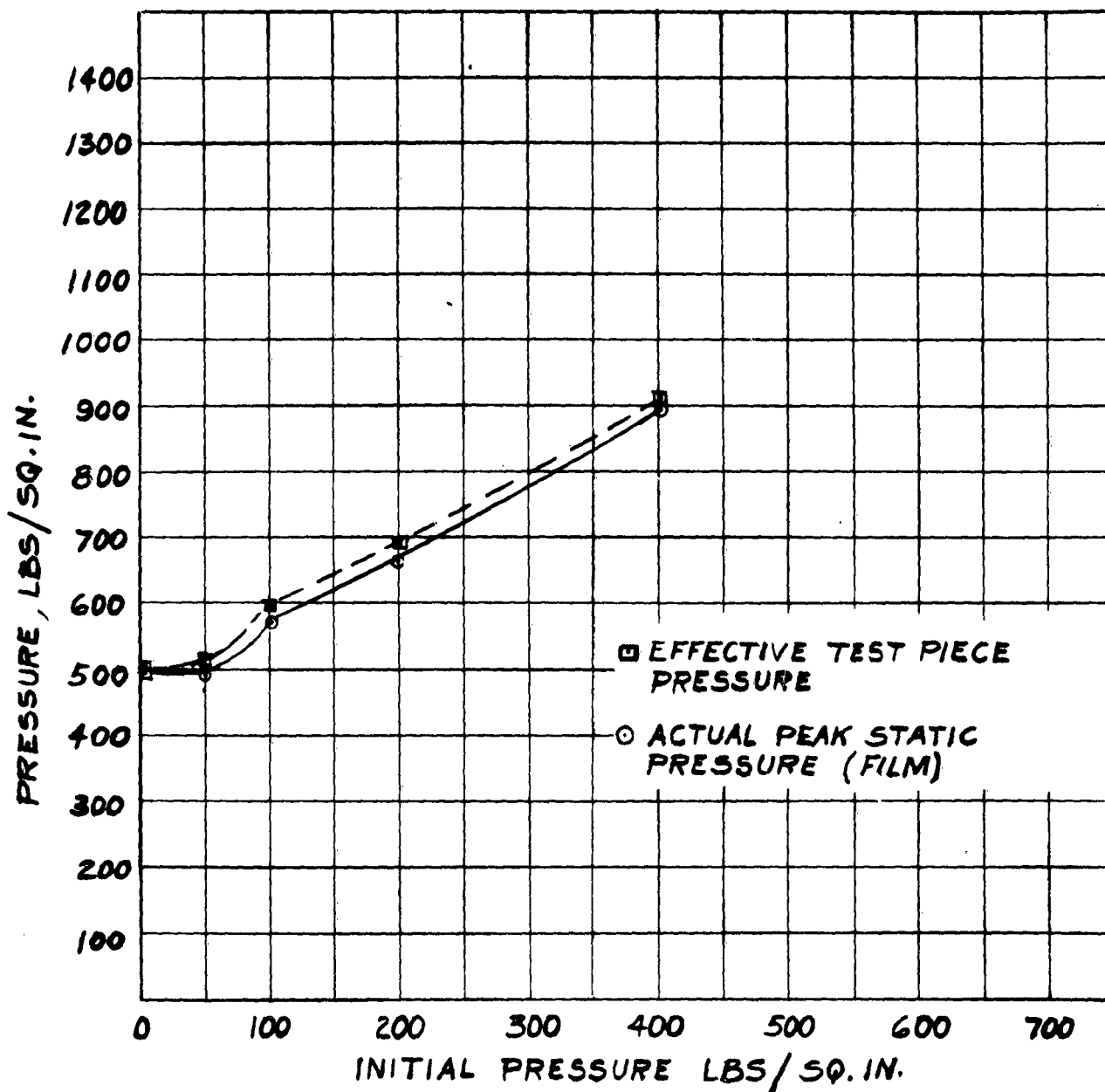


FIG 17 PLOT OF THE EFFECTIVE TEST PIECE PRESSURE AND THE ACTUAL PEAK STATIC PRESSURE (FROM FILM STRIP) ALL RUNS SET TO GIVE A FINAL PRESSURE RISE OF 400 p.s.i.

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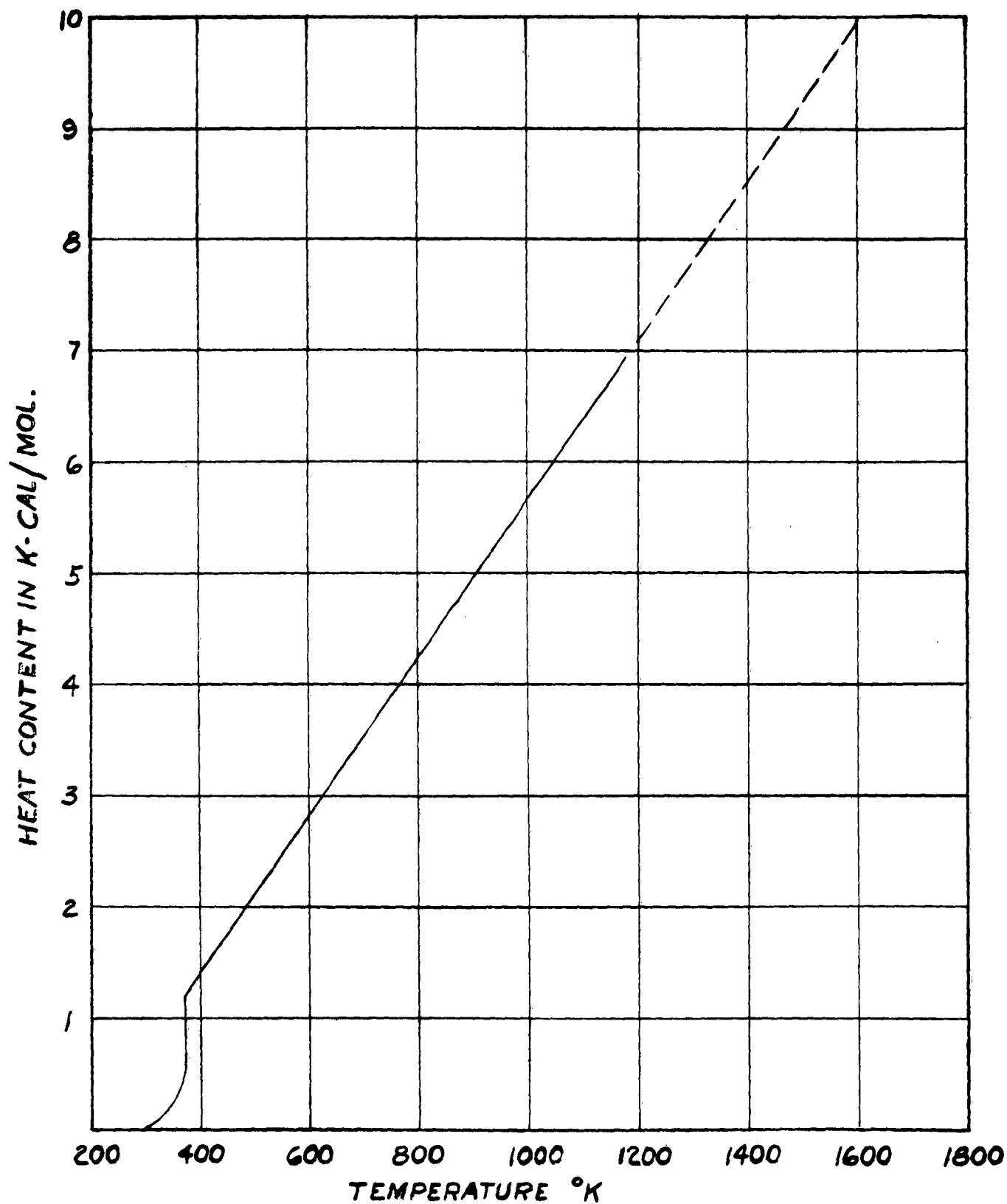


FIG 18 TOTAL HEAT CURVE FOR Na ABOVE 291 °K
DATA TAKEN FROM (6)

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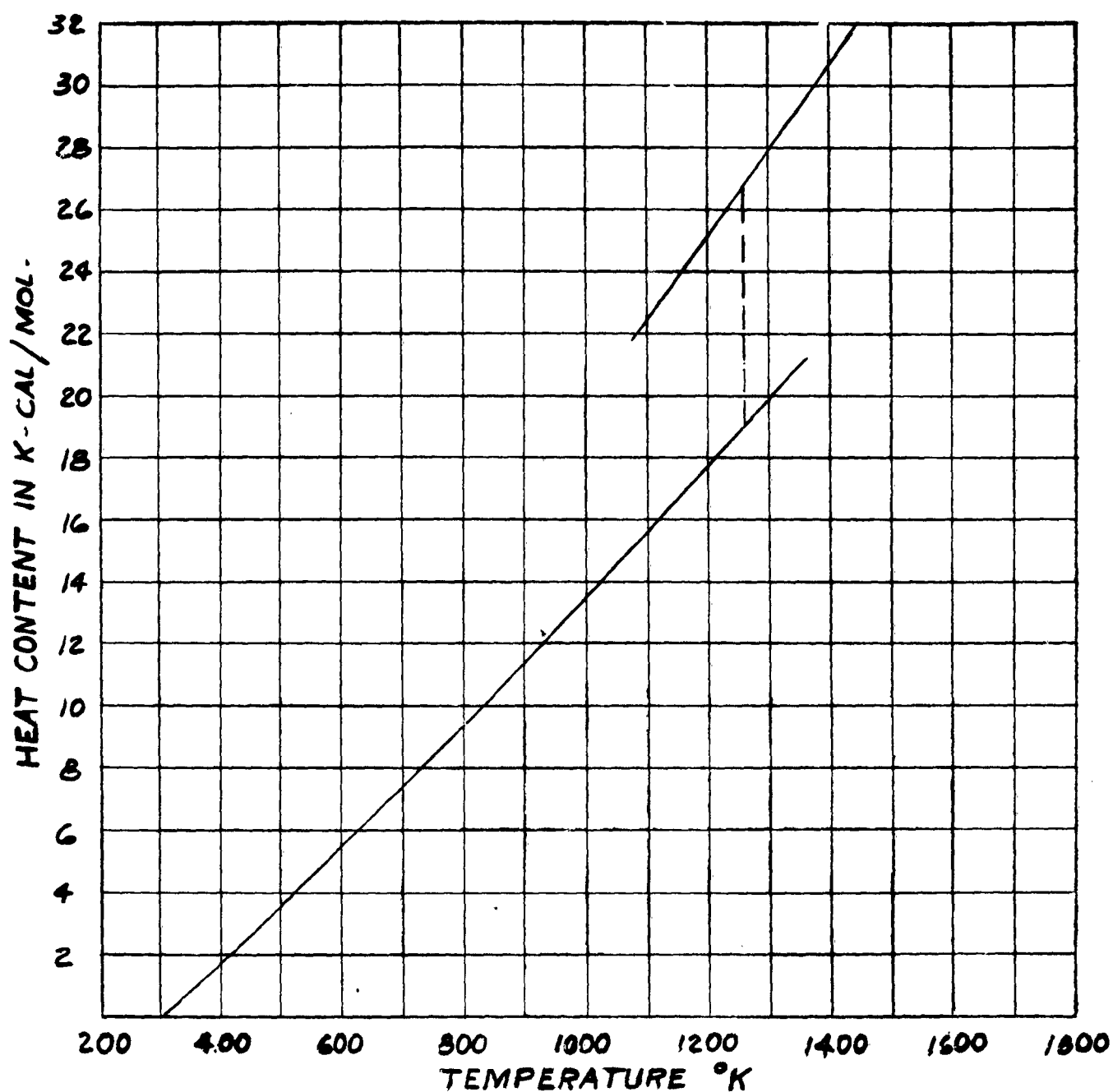


FIG 19 TOTAL HEAT CURVE FOR Na_2O ABOVE 291 °K.
THE DATA IS EXTENDED BY CALCULATIONS PAST
THE TRANSION RANGE (7)

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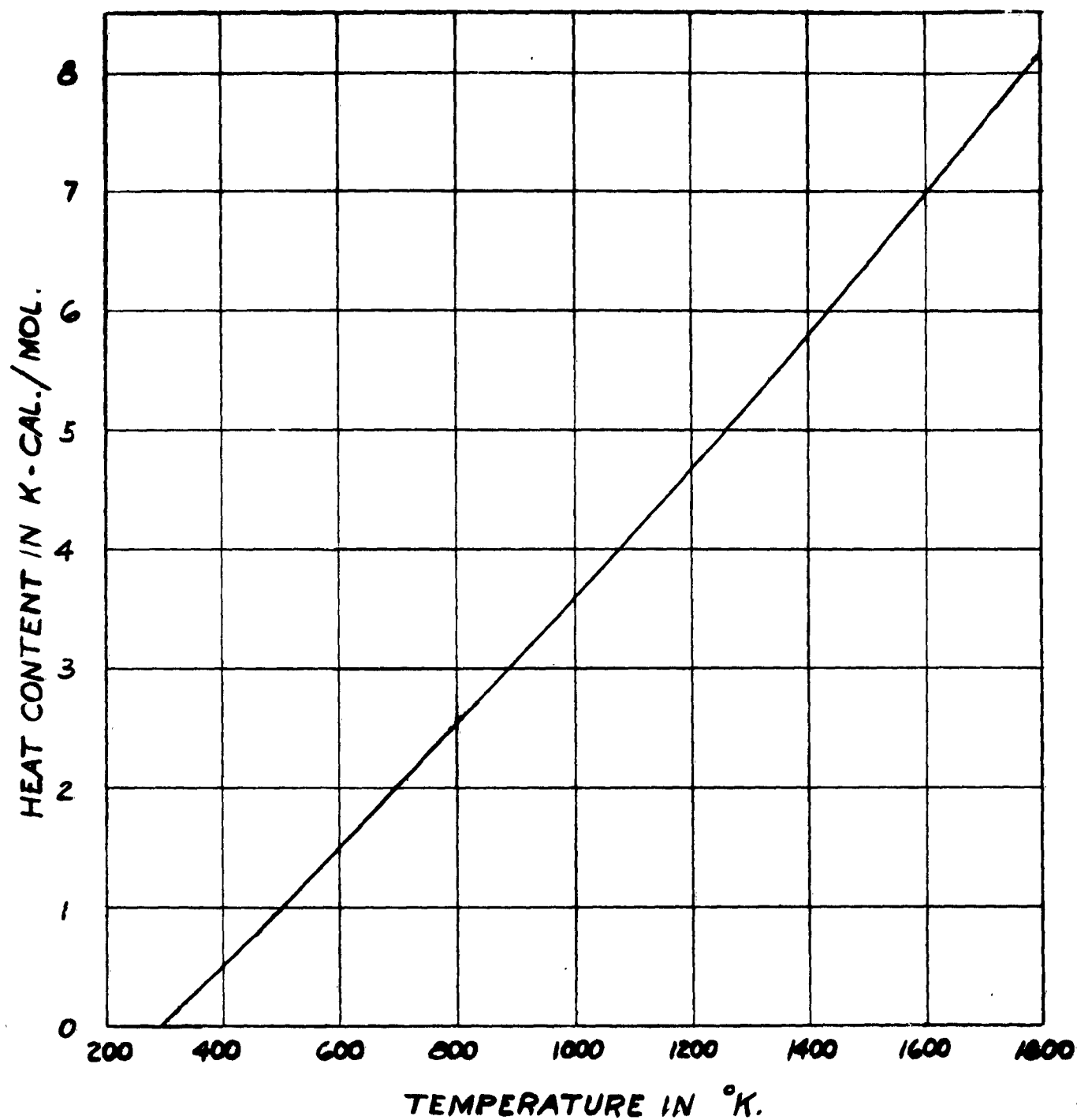


FIG. 20 TOTAL HEAT CURVE FOR H_2 ABOVE 291 °K
DATA FOR SP. HT. TAKEN FROM (8)

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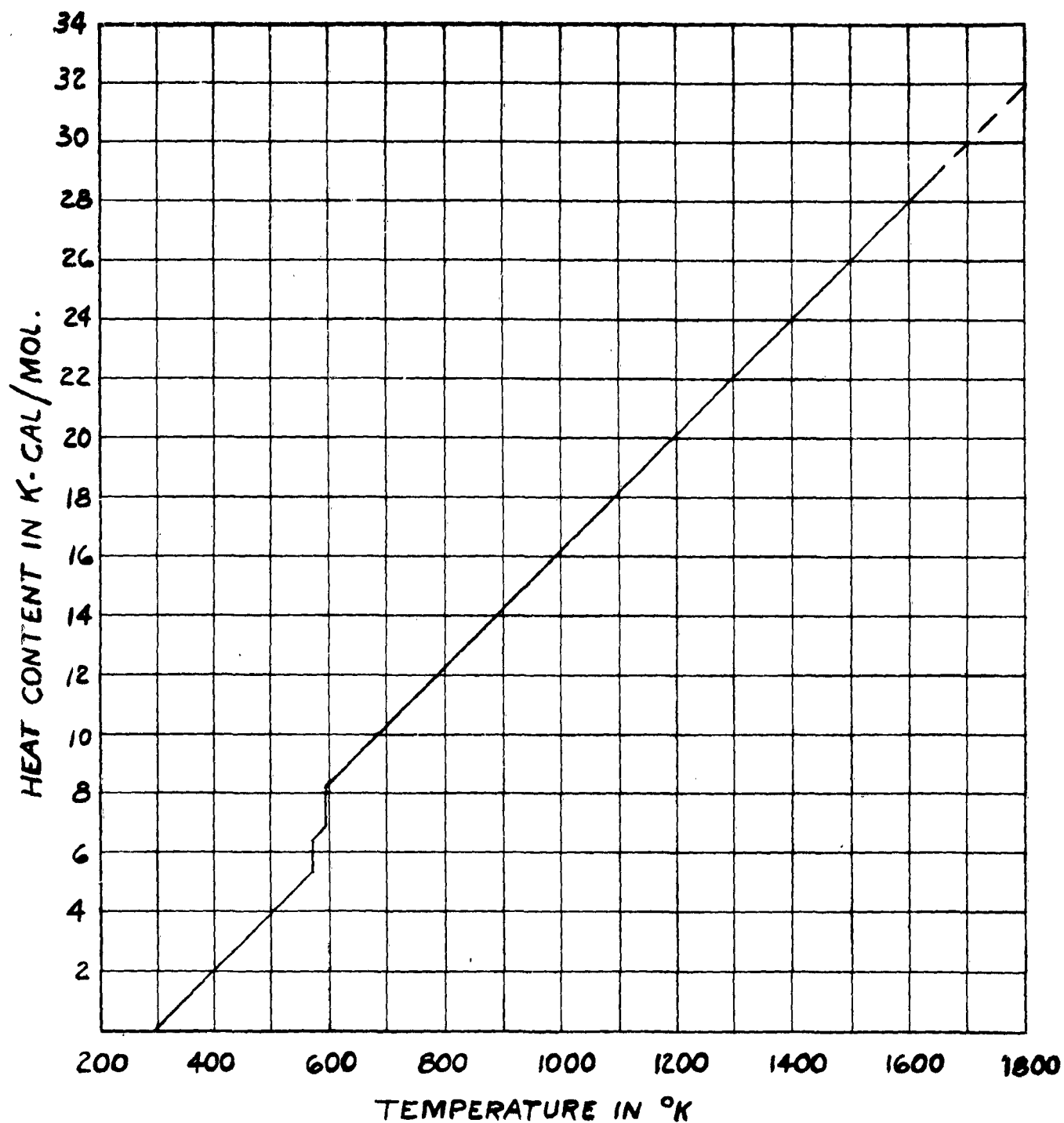


FIG 21 TOTAL HEAT CURVE FOR NaOH ABOVE 291°K
 ASSUMING:
 THE SP. HT. OF NaOH TO BE .4854 (9)
 HEAT OF TRANSION 990 CAL/MOL. AT 572°K (10)
 HEAT OF FUSION 1602 CAL/MOL. AT 591°K (10)

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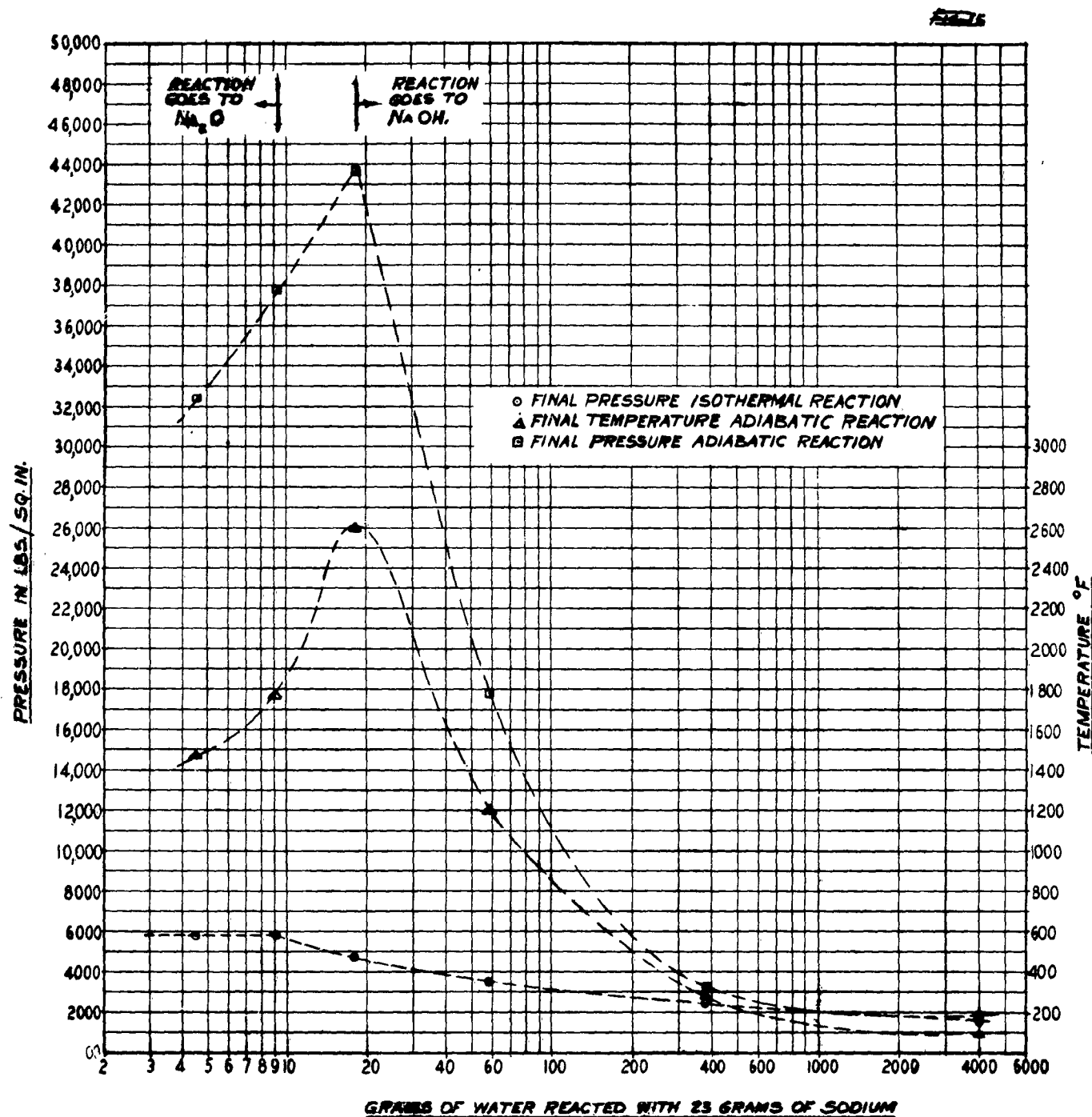


Fig. 22

ESTIMATED FINAL PRESSURE AND TEMPERATURE RESULTING FROM THE REACTION OF Na & H_2O AT AN INITIAL TEMPERATURE OF 18°C AND 1 ATMOSPHERE PRESSURE

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